FIRST-PRINCIPLES-BASED KINETIC MODELING OF BRØNSTED AND LEWIS ACIDIC ZEOLITES FOR THE CATALYTIC CONVERSION OF FURANS TO AROMATICS

by

Ryan E. Patet

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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ABSTRACT

Polyethylene terephthalate (PET) plastics and fibers are produced through the reaction of terephthalic acid with monoethylene glycol. Current renewable PET products can only claim to be 30% renewable, as the terephthalic acid which makes up *ca.* 70% of its structure is still derived from petroleum sources. In order to achieve 100% bio-derived PET materials, a renewable route to terephthalic acid is needed. The discovery that biomass-derived furans and ethylene react to form aromatics over solid acid zeolites has provided a potential pathway for the renewable production of terephthalic acid.

Computational studies of this system revealed a tandem reaction scheme, whereby furans and ethylene undergo a concerted Diels-Alder cycloaddition to form an oxanorbornene intermediate, which successively dehydrates to an aromatic. The role of Brønsted acidic zeolites has been shown, through first-principles density functional theory (DFT) calculations, to be on the dehydration reaction of the tandem scheme.

Direct comparisons between these DFT calculations and experimental observations have remained a challenge, due to the complicated nature of these systems, however. Experimentally, interesting behaviors were observed, whereby adding catalyst to the reactor caused an increase in aromatic production rate at low catalyst loadings, but had no effect on the rate at high catalyst loadings. Additionally, studies extended beyond well-understood Brønsted acidic zeolites to framework-substituted Lewis acid zeolites demonstrated this same behavior.

In this dissertation, DFT calculations are connected to experimental observations through the parameterization of microkinetic models of the reactor systems. A systematic approach is taken to create combined quantum mechanical, molecular mechanical model of zeolite active sites and the surrounding pore, which significantly improves the accuracy of adsorbate interactions with zeolites, without significantly increasing the computational costs. These improved zeolite models are used to parameterize microkinetic models of Brønsted acidic zeolites, providing fundamental explanations for the aforementioned experimental observations, but also to investigate the fundamental role of Brønsted acid strength in reactivity of these materials.

A study of Sn, Ti, and Zr, framework-substituted zeolites provides insights into the role of the active site of these materials for the aromatization of furans. The ability to isolate elementary reaction steps computationally is used to investigate the effects of Lewis and Brønsted acid sites in these materials on the Diels-Alder cycloaddition and dehydration reactions separately. Their overall contributions to furan aromatization are also examined. Finally, framework-substituted, Zn-containing zeolites are studied for their ability to catalyze the aromatization of oxygenated furans. Little is known about the active site in these materials, and so possible structures are explored for their intrinsic properties and their effect on reactivity.

Chapter 1

INTRODUCTION

1.1 Motivation

1.1.1 The energy and chemicals landscape

It is impossible to discuss the state of the chemicals and energy industry without acknowledging the important role that fossil resources play. According to BP's Statistical Review of World Energy from 2016, oil, coal, and natural gas accounted for *ca.* 85% of world energy consumption in 2015, with the remaining 15% produced by hydroelectric, nuclear, and other alternative energy sources [1]. Of the fossil resources, coal and natural gas (accounting for *ca.* 50% of world energy demand) are generally used for heating and electricity generation. Depending on the region of the world, crude oil is used for the same purpose, but more commonly is refined into a range of distillates used to produce transportation fuels (*e.g.* gasoline and diesel), waxes and tars, and chemicals [1, 2].

Differences between these fossil resources and their uses can be understood by examining their chemical composition – notably, their hydrogen to carbon (H/C) ratio [2]. Most liquid fuels and industrial chemicals have an intermediate H/C ratio of *ca*. 1.5-2.5 [2]. Crude oil, with an H/C ratio of 1.6, has a chemical composition closest to these products, making it an ideal source for their production [2]. Coal has a lower hydrogen content (H/C ratio *ca*. 0.5-1), requiring the addition of hydrogen to reach the desirable range for fuels and chemicals, while natural gas has an excess of hydrogen (H/C ratio

3.5-4), requiring its removal [2]. The high H/C ratio of natural gas has made it the primary resource for hydrogen and syngas production through steam methane reforming [3]. The high heating values of natural gas and coal (*ca.* 5-12 kcal/g), make them excellent combustion fuels for heating and electricity generation [2].

Concerns about the sourcing, availability, and their environmental impact of fossil resources has spurred research into viable alternatives [1, 2, 4]. In 2014, of the 15% of net energy consumption not produced by oil, coal, or natural gas, *ca*. 50% came from sources that provide no organic material, such as hydroelectric, wind, nuclear, and solar energies [1, 2, 5]. Of the remaining contributors, *ca*. 30% came from the burning of wood and wastes and *ca*. 20% came from biofuels (*e.g.* bioethanol and biodiesel) [5]. Biofuels are unique in this list, in that they result in a tangible liquid product at the end of processing, as opposed to simply providing a source of heat or electricity. This helps biofuel overcome one of the major challenges facing the alternative energy field; the requirement of batteries to store the electricity generated when intermittent sources (*e.g.* wind and solar energy) are not available or for mobile applications [6, 7].

Despite the impact of biomass on liquid fuels, its potential becomes even more significant when considering its unique potential for the chemicals industry. Its H/C ratio of 1.2-1.7, is very similar to that of crude oil used to produce industrial chemicals [2, 4, 5]. It is estimated that *ca*. 6 million dry tons of corn and soy beans (less than 2% of total crop production) were processed into chemicals in 2014, with the majority of this production going towards the aforementioned biofuels [5]. These existing bioethanol and biodiesel production routes largely utilize the starchy part of the plants, placing them in direct competition with food production [4, 8]. Significant enhancements in biomass utilization could be achieved if the inedible portions of

existing lignocellulosic biomass feedstocks (*e.g.* the woody parts of trees) could be leveraged and if products beyond liquid fuels were targeted [4, 5, 8]. Efforts in these areas have been slowed by increased chemical complexity of these lignin sources and the more restrictive purity standards needed to produce chemicals [4, 5, 8].

Extensive research has been targeting ways to overcome the barriers presented by the processing of lignocellulosic biomass. Methods to convert biomass from a solid to useful liquid fuels and chemicals include high temperature routes such as gasification and pyrolysis to a mixed bio-oil, as well as lower temperature alternatives such as acid hydrolysis, enzymatic hydrolysis, or aqueous phase reforming [4, 8]. In order for these processes to compete with fossil resources, further improvements are needed in the areas of product selectivity and separation. Research into catalysts tailored for these applications has provided promising new potential pathways towards this end [4, 8].

1.1.2 Producing biomass-derived plastics

Given its higher cost of acquisition and processing, high value or volume chemicals must be targeted to compete with fossil resources. Terephthalic acid (TPA) meets this requirement due to its use in the high volume production of polyethylene terephthalate (PET) plastics and fibers [9, 10]. Approximately 57 million tons of PET was produced in 2012, with capacity projected to increase to 83 million tons by 2018 [9, 10].

The PET polymer is produced through a condensation reaction between mono ethylene glycol (MEG) with TPA (Figure 1.1). "Green" PET plastics do exist in the marketplace, although only the MEG monomer is sourced from biomass sources, comprising only *ca*. 30% of the final polymer [9, 10]. The TPA monomer, making up



Figure 1.1. Reaction scheme for the production of PET from *p*-xylene.

the remaining *ca.* 70% of PET, is derived from the naphtha portion of petroleum by oxidizing p-xylene (pX) by the AMOCO process (Figure 1.1) [9-13]. In order to achieve 100% renewable PET, a viable route to TPA from biomass is needed.

Progress has been made towards the production of renewable TPA with the discovery of a solid acid-catalyzed reaction of biomass-derived furans and ethylene to aromatics [14-21]. Renewable alkylated furans can be produced from the hydrodeoxygenation of biomass-derived furfural and hydroxymethylfurfural, and ethylene from the dehydration of bioethanol [22-24]. The subsequent aromatization of these bio-derived reactants is known to proceed through tandem Diels-Alder cycloaddition and dehydration reactions (Figure 1.2) [19]. Solid acids are known catalysts for these reactions, with the highest activity and yields of aromatics achieved when using zeolites [20, 21, 25].



Figure 1.2. Reaction scheme for the production of aromatics from furans and ethylene.

1.1.3 Computational modeling of furan aromatization: State of the field and future outlook

Computational studies of acid catalysts have been used to investigate their catalytic effect on the aromatization of furans [19, 26, 27]. In these studies, density functional theory (DFT) calculations of Brønsted and Lewis acid catalyzed reaction profiles involving gas-phase [19, 26] or zeolite embedded [27] cations have been compared to uncatalyzed, gas-phase reactions. In the uncatalyzed reaction of 2,5-dimethylfuran (DMF, $R_1=R_2=CH_3$ in Figure 1.2) with ethylene to *p*-xylene the Diels-Alder cycloaddition reaction has a barrier of *ca*. 40 kcal/mol and the dehydration reaction, represented the rate-limiting step, has a barrier of *ca*. 60 kcal/mol. In the presence of a Brønsted acidic proton, the Diels-Alder reaction barrier remains unaffected while the dehydration barrier decreases to *ca*. 12-19 kcal/mol. The role of Brønsted acids are as dehydration catalysts in the tandem aromatization scheme.

Homogeneous Lewis acids are known Diels-Alder reaction catalysts, and therefore the ion-exchanged (Li-, Na-, K-, Rb-, and Cs-FAU) Lewis acid zeolites have also been studied as potential Diels-Alder catalysts [26-28]. Calculations performed with gas-phase cations showed a potential decrease in the Diels-Alder cycloaddition barrier by *ca*. 7 kcal/mol when the strongest Lewis acid cation, Li⁺, coordinated to

ethylene during the reaction [26]. When Li^+ coordinated with DMF, however, that barrier was only decreased by *ca*. 2 kcal/mol. The situation worsened when these cations were embedded in a zeolite framework [27]. In these models, the ethylene-mediated reaction only decreased by *ca*. 3 kcal/mol and the DMF-mediated reaction barrier decreased by *ca*. 1 kcal/mol. The embedding of these cations into the zeolite framework causes a shielding of the effective positive charge of the cations by surrounding zeolite framework oxygen atoms, reducing their potency as Lewis acids. In addition, dehydration barriers with these Lewis acid active sites were significantly higher (38-54 kcal/mol) than their Brønsted acid counterparts.

In spite of the success of these fundamental studies towards understanding the role of solid acid catalysts for furan aromatization, direct quantitative comparisons to experiments remain a challenge. In calculations involving gas phase ions or small quantum clusters of zeolite active sites cut from the extended framework, the surrounding zeolite pore is not accounted for [19, 26, 27]. The calculations of intrinsic reaction barriers benefit from a cancellation of errors, whereby an extended zeolite model would affect ground state and transition states alike. Errors arise, however, when attempting direct comparisons to experiments, where the extended zeolite framework can have a significant effect on the adsorption properties of molecules.

In addition, new catalytic zeolites have been discovered, capable of catalyzing the aromatization of furans [29-33]. These materials contain framework-substituted metal atoms (Sn, Ti, Zr, and Zn) which are fundamentally different from the ionexchanged systems studied to this point. Relatively little is known about the potential Brønsted or Lewis acidic nature of the active sites in these materials and their role as catalysts for the aromatization of furans. Fundamental computational studies into these catalysts can provide new insights into the nature of their active sites and into the fundamental understanding of the role of Brønsted and Lewis acids as catalysts in the aromatization of furans.

1.2 Computational Methods

1.2.1 Quantum calculations

In theory, quantum mechanics provides exact solutions to the calculation of electronic energies through the solution of the Schrödinger equation [34]. In practice, the only known exact solution to this equation is for the hydrogen atom with a single electron – and even that solution involves approximations, such as the Born-Oppenheimer approximation that the motion of protons are much slower than the motion of electrons, owing to their significantly larger mass, and therefore are treated as stationary. The presence of even a single additional electron leads to uncertainty in the calculations, due to the interaction of the electrons with one another.

Without an exact solution available, useful approximations have been derived capable of calculating the desired electronic properties [34]. The Hartree-Fock self-consistent-field method represents one of the simplest approaches to this problem. By this method, approximate wavefunctions are guessed for each electron and improved through iterative methods until some convergence criteria is met. Fundamentally, this approach treats each electron of the system individually and, as previously mentioned, cannot calculate the exact interaction between these electrons.

Another approach to handling the uncertainty of electronic interaction is density functional theory (DFT), as described by the Kohn-Sham formalism [34-36]. The Kohn-

Sham formalism states that the total energy of a system can be described as a functional of the electron density,

$$E[\rho] = -\frac{1}{2} \sum_{i=1}^{n} \int \Psi_{i}^{*}(r_{1}) \nabla_{i}^{2} \Psi_{i}(r_{1}) dr_{1} - \sum_{X=1}^{N} \int \frac{Z_{X}}{r_{X_{i}}} \rho(r_{1}) dr_{1} + \frac{1}{2} \int \int \frac{\rho(r_{1})\rho(r_{2})}{r_{12}} dr_{1} dr_{2} + E^{XC}[\rho]$$

$$(1.1)$$

where the energy, as calculated by the electron density functional, is the sum of the first term calculating the kinetic energy of non-interacting electrons, the second term calculating the interaction between nuclei and electrons, the third term calculating the repulsion of nuclei, and the final term, the exchange-correlation functional. By the Kohn-Sham formalism, rather than treating each electron individually, they are grouped into an effective electron density.

Although it has solved the interaction problem of individual electrons, the Kohn-Sham approximation still does not provide an exact solution. The electron density at a given point in space is affected by the overall electron density of the system, as accounted for by the exchange-correlation functional [34-36]. In general, differences in density functional theories come from how they address the issue of the exchange-correlation functional. Local density approximation methods (LDA, *e.g.* SPWL) treat the exchange-correlation energy at any point in space as a function of the electron density at that point alone, generalized gradient approximation methods (GGA, *e.g.* BLYP, PBE) treat the exchange-correlation energy at any point in space as a function of the density and the gradient of the density at that point, hybrid GGA methods (*e.g.* B3LYP) incorporate percentages of Hartree-Fock exchange with conventional GGA methods, and hybrid meta-GGA methods (*e.g.* M06-2X, ω B97XD) incorporate empirical fitting to hybrid GGA methods. This collection of theories represents both the

progression in the development of DFT approximations as a survey theories still used depending upon the size of the system, its constituent atoms, and the speed and accuracy required of the calculations. Choosing the best theory level for a set of calculations represents the first step towards accurately calculating the electronic properties of a system.

Second, a choice of basis sets to describe the molecular orbitals of the system must be made [34]. Again, without an exact solution to the Kohn-Sham approximation, approximations must be made about the functionals used to represent the electron density. Two ways of defining a system are to treat it as a periodic system, where its functionals span the defined space of the model, or as an atomic system, where its functionals are centered about the individual atoms. In the latter case, molecular orbitals are approximated as a combination Gaussian-type functions. Minimal basis sets treat each orbital as a single function, double-, triple-, and quadruple-zeta basis sets treat each molecular orbital as a combination of 2, 3, and 4 functions, respectively, and splitvalence basis sets treat core electrons with single function and valence shell electrons with a combination of functions. Splitting orbitals into a combination of Gaussian functions allows the calculations to remain fairly quick, due to the simplicity of the Gaussian function, while allowing different combinations create molecular features. Proper parameterization can lead to directional polarization, useful for directional bonding, and diffuse functionals, which fall off slowly as the distance from the nucleus increases and capture extended dispersion forces.

The choice of a DFT level of theory and basis set represents an important factor for any computational chemist. In general, increasing the complexity of the method or the size of the basis set provides a means to improve the accuracy of the calculations, at the expense of computational time. When starting a study into any new set of chemistries, it is useful to try a variety and methods and basis sets to gauge their relative importance on the accuracy of the results, and then determine the best tradeoff between speed and accuracy.

1.2.2 ONIOM methodology

Sometimes, a system becomes too large to be treated entirely by DFT methods, due to cubic scaling of these calculations with the number of atoms in the system [34-36]. In these types of systems, a hybrid approach may be employed. The embedding of quantum mechanical layers into a larger molecular mechanics layer represents one approach to this problem. Rather than treating the entire system with accurate but expensive DFT calculations, only the region of the system of greatest importance needs to be treated at this level of accuracy (quantum layer). The remaining atoms can be calculated by more approximate methods as a way of speeding up the calculations (molecular mechanics layer).

One implementation of this approach is the ONIOM method (our own *n*-layered integrated molecular orbital and molecular mechanics) [37]. A summary of the approach can be seen in Figure 1.3 for a 3-layered ONIOM model. The vertical axis represents the qualitative accuracy of the theory level of the calculation and the horizontal axis represents the qualitative size of the system. Ideally, at the point of the star in the top right, the entire system (Real) would be calculated at the highest theory level (High). Because this is not possible, the three-layer scheme involves a series of five calculations to approximate this values (represented by the filled and unfilled circles on the diagram). The small layer is treated at both the high and medium theory levels, the intermediate


Figure 1.3. Representation of the ONIOM methodology.

layer is treated at both the medium and low theory levels, and the real layer containing all of the atoms at the low theory level (generally a molecular mechanics theory). These values are used to calculate a 3-layer ONIOM approximation of the energy of the system E(ONIOM3) = E(H,S) - E(M,S) + E(M,I) - E(L,I) + E(L,R) (1.2) Or, using the letter representations in Figure 1.3: $E(ONIOM3) = E(H,S) + \sim D + \sim C$ (1.3)

or

$$E(ONIOM3) = \sim A + \sim B + E(L,R)$$
(1.4)

This three-layer approach can be more generally applied systems containing two or more layers, with a commensurate number of calculations to step up to the approximate ONIOM value [37]. The accuracy of the method is, obviously, dependent on how accurately the approximations of changing the theory levels of systems of different sizes, or the sizes of systems of different theory levels, represents the true difference in energy. When trying to understand the application of the ONIOM methodology to new systems, changing to the theory level *and* to the size of the layers to gauge their effect on the calculated parameters is useful to understanding their overall importance for accuracy and computational time.

1.2.3 Kinetic reactor modeling

Microkinetic modeling provides a means to translate insights from the molecular length and time scales to those of a macroscopic reactor model [38]. Therefore, construction of the model must consider both scales in its implementation. At the macroscopic level, different reactors (*e.g.* batch, CSTR, PFR) can be modeled by choosing the appropriate design equation and accounting for the sources and sinks of the system [39]. At the microscopic scale, a series of elementary steps is selected to define the chemistry of interest. By considering all elementary steps, no assumption need be made about rate-limiting or quasi-equilibrated reactions. Failing to accurately represent all of the relevant elementary steps of a reaction, however, can lead to significant errors in the predicted rates and product selectivities.

To link the microscopic and macroscopic scales, the elementary reaction steps are translated into a series of kinetic reaction steps, organized into a set of differential equations. Kinetic parameters for these systems can be estimated by the Eyring equation as:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^*}{RT}}$$
(1.5)

where the Gibb's free energy of reaction can be calculated through DFT calculations, by other approximate methods (*e.g.* BEP relations, group additivity), or through experimental measurements [38-40]. With these differential equations defined, an appropriate solver can be used to solve the systems of equations. By manipulating the input variables to the model (*e.g.* temperature, pressure, concentrations, time), product concentrations, reaction rates, apparent reaction barriers, and reaction orders can all be calculated for direct comparison to experiments. Tools such as reaction path analysis provide insights into the most relevant reaction pathways and sensitivity analysis helps to determine the most important catalytic steps affecting a given rate. In addition, properties such as catalyst coverage or intermediate concentrations, inaccessible to experiments, can be calculated by these models.

Microkinetic models represent a powerful way to link fundamental energy calculations to experimental observations at the macroscopic scale. The combination of analysis tools allows for a feedback loop, whereby the two systems can be used to improve one-another [38]. The iterative process between these scales leads to better models at both ends.

1.3 Dissertation Scope and Overview

The body of this thesis is comprised of two major sections divided into five body chapters. In the first section (Chapters 2, 3, and 4), studies are performed on Brønsted acidic zeolites and in the second section (Chapter 5 and 6) two distinct classes of framework-substituted Lewis acid zeolites are investigated.

Before having confidence in our ability to create reactor models for comparison to experimental systems, accurate computational models of our catalysts are needed. In Chapter 2, a systematic study is performed investigating the adsorption strength of a range of organic molecules in H-MFI, H-BEA, and H-FAU zeolites. The mechanical embedding of quantum mechanics layers within a larger molecular mechanics layer by the ONIOM methodology is used to construct zeolite models with information about the local active site and surrounding zeolite pore. Significant improvements in the calculated adsorption strengths of the studied adsorbates are achieved, providing a model with the accuracy needed to build microkinetic models.

In Chapter 3, we set out to investigate an intriguing set of experimental observations made by Prof. Wei Fan's and Prof. Paul J. Dauenhauer's groups. Two distinct catalytic regimes were identified for the aromatization of 2,5-dimethylfuran and ethylene to *p*-xylene; a low acid site concentration regime where the addition of catalyst caused a commensurate increase in reaction rate and a high acid site concentration regime where the rate was independent of the acid site concentration. We used ONIOM models of Brønsted acidic zeolites to parameterize microkinetic and a reduced kinetic models capable of replicating these experimental observations. These two kinetic regimes are shown to be due to the uncatalyzed first step (Diels-Alder cycloaddition) and catalyzed second step (dehydration) of the tandem reactions for these aromatization reactions. Experimental results shown in this chapter were gathered by Dr. C. Luke Williams, Dr. Sara K. Green, and Dr. Chun-Chih Chang.

In Chapter 4, the role of Brønsted acid strength on activity and selectivity is investigated by modifying substituent atoms in BEA zeolites. Reactions of furan, 2-methylfuran, and 2,5-dimethylfuran over Al-, Fe-, Ga-, and B-substituted zeolites are used to probe the reactivity of these materials. Interestingly, the weakest acid in this series, H-[B]-BEA, is predicted to be as reactive as the strongest acid, H-[Al]-BEA, for the aromatization of furans using ONIOM calculation parameterized microkinetic models, as confirmed by experiments run by Maura Koehle of Prof. Raul Lobo's group.

In Chapter 5, the experimental discoveries of the Davis group [29, 30] and the Fan group [31, 32] of improvements in the selectivity to aromatics over of Sn-, Ti-, and

Zr-BEA. ONIOM models are constructed of a "closed" active sites, where the metal atom is tetrahedrally coordinated to the surrounding framework oxygens and an "open" active site, hydrolyzed by water, and investigate their role as Brønsted or Lewis acidic materials. A microkinetic model predicts, for the first time, a Lewis acid catalyzed pathway as a dominant pathway for furan aromatization.

An ongoing study is presented in Chapter 6, on the recent experimental discoveries made by Orazov and Davis [33] of the catalytic activity of framework-substituted Zn-BEA materials towards the aromatization of oxygenated furans. Little is known about the active sites of these materials, therefore models are constructed to investigate the active site properties and catalytic activity. Differences in activity are determined for two different active site structures studied, as well as based on the oxygenated substituents on the furan.

Finally, in Chapter 7, overall conclusions are drawn and used to discuss potential future directions.

Chapter 2

ADSORPTION IN ZEOLITES USING MECHANICALLY EMBEDDED ONIOM CLUSTERS

2.1 Introduction

Zeolites are among the most widely studied inorganic materials. Their wideranging industrial applications (*e.g.*, separations, catalysis) [41, 42] have stimulated work which aims at optimizing the properties of existing zeolites *via* framework atom modifications, or at designing new zeolite-based materials for specific applications [41, 43-45]. Electronic structure calculations, molecular dynamics, and Monte Carlo simulations have provided tremendous insights into the properties of these materials, host-guest interactions, and catalytic activity [46-49]. Accurate description of sitespecific binding is critical to the calculation of catalytic pathways and the development of new catalysts but remains a challenge for theoretical models because the host-guest interactions are determined by long-range electrostatic interactions and the long-range electron correlation effects that give rise to dispersion forces.

Periodic density-functional theory calculations can adequately address the electrostatic problem, but LDA and GGA functionals fail to capture the rather weak dispersion forces and advanced, meta-hybrid functionals (with demonstrated ability to capture dispersion, *e.g.*, M06-2X or ω B97X-D) are not easy to utilize because of algorithmic difficulties in computing the exact exchange. Although empirical dispersion corrections (DFT-D) [50] have been parameterized for various GGA functionals, and more accurate semilocal exchange functionals (vdW-DF2) are being developed

designed to capture dispersion interactions in a non-empirical fashion, [51] periodic-DFT calculations remain computationally expensive for zeolites (cubic scaling with the number of atoms), especially if one wishes to map out catalytic pathways.

While it is widely recognized that the extended aluminosilicate framework around the active site of a zeolite-based catalyst is as important for the description of site-specific binding as the active site itself, it has also been argued that quantum mechanical description of atoms far from the active site and the substrate might not be critical. Hybrid QM/MM approaches capitalize on this premise in order to reduce the computational cost by layering the extended system (active site and a large part of the framework) into regions that are treated with varying degrees of accuracy [52-54]. These layering strategies are in essence subtractive computational schemes, whereby the low-level-theory energy of an individual layer is subtracted from the energy of the real system and is substituted by a high-level-theory estimate. Typically, the reactive region is treated quantum mechanically (QM) and the surrounding environment is treated with a molecular mechanics force field (MM). However, it is not unusual to treat the environment quantum mechanically as well (QM/QM), either with low-level theories or with periodic-DFT, with concomitant increase in the computational cost. Notable in this respect is the QM/QM strategy of Tuma and Sauer (MP2/CBS:DFT + dispersion), whereby a small-size cluster is used to model the reactive region at the MP2 level, while the rest of the system is treated with periodic-DFT [55, 56]. This strategy has the advantage of handling long-ranged electrostatic interactions more accurately and of ameliorating the problem of GGA functionals not capturing dispersion interactions. One can surely envisage the development of variants with MP2 replaced by meta-GGA

or hybrid-meta-GGA functionals specifically developed and parameterized to take into account dispersion and hydrogen bonding.

Hybrid QM/MM methodologies are inherently approximate as they primarily aim at routine applicability in large systems (*e.g.*, enzymes, zeolites). The size of the QM domain, the theory level at which the QM domain is treated, the size of the overall system, the complexity of the MM force field or of the low-level quantum theory (*e.g.*, Hartree-Fock (HF) or semi-empirical) in the environmental domain, and the interaction between the layers (*e.g.*, mechanical *versus* electrostatic embedding) are all the result of a compromise between accuracy and computational efficiency. Choices that work universally remain a challenge. For example, what works for non-polar probe or substrate molecules might not work as well for polar ones, or when the adsorbate is basic enough to deprotonate proton-exchanged zeolites, leading to formation of an ionpair structure.

Two-layer QM/MM studies with small, high-theory layers and medium-size, low-theory layers (containing on the order of 50 tetrahedral atoms or 50T) have been valuable at demonstrating capabilities and exposing limitations [57-71]. ONIOM(B3LYP/6-31++G(d,p):HF/3-21G)single point calculations on ONIOM(B3LYP/6-31++G(d,p):MNDO) optimized structures of a (12T:48T) cluster model of acidic CHA for the adsorption of H₂O and NH₃ correctly predict proton donation to NH₃ and ion-pair formation [65]. A comparison of computed binding energies with experimental data was not made, but one expects that the deviation from experiment should be significant given that B3LYP does not capture dispersive and hydrogen-bonding interactions. The binding energy was, nonetheless, in satisfactory agreement with periodic-B3LYP calculations – albeit somewhat underestimated – which is remarkable considering the rather small size of the embedded cluster and the level of theory at which the outer-layer was modelled (HF/3-21G). Nevertheless, the reasonable agreement between periodic-B3LYP calculations and ONIOM(B3LYP/6-31++G(d,p):HF/3-21G//B3LYP/6-31++G(d,p):MNDO) suggests that the electrostatic interactions are rather well captured, although, convergence with the outer-layer basis set size was not reported and thus we are unable to assess the role of error cancellation in the ONIOM estimates. Interestingly, when the same methodology was applied to a host of probe molecules within a wide range of proton affinities (*i.e.*, gas-phase basicities) and compared with experimental data, the binding was severely underestimated, especially that of ion-pairs [64].

Boekfa *et al.* have used a 5T:34T embedded model of H-MFI and computed binding energies for ethylene, benzene, ethylbenzene, and pyridine considering a combination of MP2 for the high-layer and various methods for the outer layer, including UFF (Universal Force Field), HF, B3LYP and M06-2X, with various combinations of triple- ζ -plus-diffuse and double- ζ quality basis sets, respectively [68]. They have asserted that ONIOM(MP2/6-311+G(2df,2p):M06-2X/6-31G(d,p)//MP2/6-31G(d,p):M06-2X/6-31G(d,p)) gives good binding energies. This assertion was based on a comparison of the computed energies with experimental energies in H-FAU and not in H-MFI (the zeolite that was actually modelled) and thus it is difficult to ascertain the accuracy of the method. In fact, the rather acceptable error of *ca.* +5 kcal mol⁻¹ (under-binding) should be expected to be higher in H-MFI, given that H-MFI has stronger acidity and smaller pores than H-FAU [72-75].

Recently, Head-Gordon and co-workers partially re-parameterized the CHARMM force field for QM/MM calculations of electrostatically embedded zeolite

cluster models [69-71]. By investigating convergence with respect to the size of the framework QM domain, they have suggested that the QM region does not have to extend beyond the first coordination sphere and proposed the use of a 5T cluster which they model at the ω B97X-D/6-311++G(3df,3pd)// ω B97X-D/6-31G(d,p) theory level (namely, optimization at the ω B97X-D/6-31G(d,p) level followed by a single-point energy calculation at the ω B97X-D/6-311++G(3df,3pd) level). Thus the burden of capturing the interaction between the substrate molecule and the framework of the zeolite is on the force field that models the MM region, typically consisting of up to 44 tetrahedral atoms. They have computed binding energies within 10% of the reported experimental values for species that are both physisorbed and chemisorbed in MFI, H-MFI, and H-BEA zeolites [71]. This is a promising methodology which has demonstrated considerable improvements in accuracy, although it remains to be tested for a wider class of polar probe molecules and whether further re-parameterization of the CHARMM force field will be required.

Having in mind wide and routine applicability, in this article we explore a mechanically-embedded, three-layer QM/QM/MM ONIOM approach which retains the simplicity of the Universal Force Field (UFF) for the MM region. Philosophically, our decision to explore a QM/QM/MM approach stems from the understanding that, for polar and strongly binding substrate molecules, the binding energy greatly depends on QM–MM interactions, dispersive, and electrostatic. Electrostatic interactions, in particular, polarize the active site (always part of the QM region) and a reliable approach toward capturing such interactions more adequately would be to replace part of the MM region with a quantum region that would be treated at a medium theory level which, nevertheless, is capable of capturing some of the dispersion interactions as well. By

considering a broad class of probe molecules, our intent is to understand the range of these interactions in the sense of how extended the intermediate layer needs to be and of the "minimal" theory level one needs to employ to describe it, while maintaining a good balance between reliability and computational cost.

2.2 Computational Methods

2.2.1 Embedded cluster design

Zeolite clusters were cut out from crystals taken from the database of structures maintained by the IZA [76]. Dangling silicon bonds from this structure were saturated with hydrogen atoms at a bond length of 1.47 Å along the corresponding Si–O bond vectors of the crystal. One silicon atom was replaced by an aluminum atom and an H⁺ cation was introduced to the adjacent oxygen atom in the lowest-energy configuration.

The QM/MM zeolite models were developed using the ONIOM method, as implemented in the Gaussian 09 suite of programs [37, 77-80]. We have investigated both two- and three-layer ONIOM models, whereby the total enthalpy of the system is given by

$$H(ONIOM2) = H(H,SL) + H(L,RL) - H(L,SL)$$
(2.1)

$$H(ONIOM3) = H(H,SL) + H(M,IL) + H(L,RL) - H(M,SL) - H(L,IL)$$
(2.2)

where H, M, and L refer to the high, medium and low levels of theory and SL, IL, and RL refer to the small, intermediate, and real layers of the system [37]. For this study, the small and intermediate ONIOM3 layers have been treated with quantum mechanical methods, while the real layer has been treated with the universal force field (UFF). The character of stationary points has been confirmed by vibrational frequency analysis.

The small layer was chosen to include the first two tetrahedral coordination spheres around the Al atom, shown for H-MFI in Figures 2.1a and b. The small layer was mechanically embedded into a real layer which includes all the atoms up to the sixth tetrahedral coordination sphere of the Al atom, again shown for H-MFI in Figures 2.1c–e. For the three-layer ONIOM models, an intermediate layer was investigated to include the third, fourth, and in the case of H-FAU, fifth tetrahedral coordination spheres around the Al atom. The real layer of the model was investigated to include the fourth, fifth, sixth, and in the case of H-FAU, seventh tetrahedral coordination spheres around the Al atom. Representations of H-MFI, H-BEA, and H-FAU can be seen in Figure 2.2. In all models, the small layer of the model was allowed to relax while the intermediate and real layers were frozen to maintain the integrity of the zeolite framework structure. We should note that, in preliminary studies, relaxation of the intermediate layer occasionally converged to structures with multiple imaginary frequencies.

2.2.2 Theory levels

In both the two-layer and three-layer models we treated the QM region with the hybrid-meta-GGA functional M06-2X, a global functional with 54% HF exchange, with demonstrated ability to capture dispersion interactions [81]. We have considered two basis sets: 6-31G(d,p) and 6-311G(2df,p). We have not considered augmented basis sets, not only because diffuse functions increase the computational cost, but also because they can increase the basis set superposition error (BSSE). Extensive studies by Truhlar and co-workers have shown that better accuracy could be achieved if the extra cost were instead invested in a larger valence space (*e.g.*, triple-zeta basis) or more polarization [82, 83].



Figure 2.1. Representations of the (a) 1st (5T), (b) 2nd (17T), (c) 3rd (40T), (d) 4th (78T), (e) 5th (137T), and (f) 6th (226T) coordination spheres surrounding an Alatom substituted in the T12 position of H-MFI.



Figure 2.2. ONIOM representations of (a) H-MFI, (b) H-BEA, and (c) H-FAU zeolites showing the layers of the standard models. The small layer is shown as a ball-and-stick representation, the intermediate layer is shown as a tubeframe representation, and the real layer is shown as a wireframe representation.

In the two-layer model, the outer (low-level) layer has been simulated with the UFF. The UFF has enjoyed significant popularity in mechanically embedded QM/MM electronic structure calculations of large systems because of its simplicity. Additionally, because of the absence of partial charges on the UFF atoms, it affords us the flexibility to partition the system into QM and MM regions in a number of ways without worrying about the net charge of the MM region not being zero. An issue that is often overlooked is that a non-neutral MM region can be a serious source of error in the binding energies, especially for polar molecules [60-63, 66-68]. We have investigated the effect of the cluster size by keeping the QM region size constant and varying the MM region. So, in the case of H-MFI, we have considered the ONIOM2 models M06-2X/6-31G(d,p):UFF and M06-2X/6-311G(2df,p):UFF and the clusters 17T:120T and 17T:209T.

In the three-layer QM/QM/MM ONIOM model, we have investigated layer size effects and theory/basis set effects for the intermediate layer while the outer layer has been simulated with the UFF. For the intermediate layer, we have considered HF theory and the three functionals B3LYP, ω B97X-D and M06-2X, the basis sets 3-21G, 6-31G, 6-311G, 6-31G(d,p), and 6-31G(2df,p), and the clusters 17T:23T:97T, 17T:61T:59T, and 17T:23T186T for H-MFI, 16T:18T:77T for H-BEA and 14T:16T:188T for H-FAU.

Calculated binding strengths have been benchmarked against available experimental values provided in Table 2.1, measured using a combination of TPD and microcalorimetry between 323 and 480 K [84-88]. Vibrational frequencies were used to calculate thermal corrections to the binding enthalpies. For the spurious soft vibrational modes of the framework and the wrong asymptotic behavior of the enthalpy at low frequencies, we have employed the quasi-rigid rotor harmonic oscillator (qRRHO) approximation proposed by Grimme [89] and Head-Gordon [71] (see Appendix A). Binding enthalpies were calculated by equation 2.3 and are reported only at atmospheric pressure and 25 $^{\circ}$ C – changing the temperature within the 50-100 $^{\circ}$ C range of experimental values changed the calculated enthalpies by less than 0.5 kcal mol⁻¹.

$$\Delta H_{ads} = H_{Z+ads} (Elec, Vib_{qRRH0}) - H_Z (Elec, Vib_{qRRH0}) - H_{ads} (Elec, Trans, Vib_{H0}, Rot)$$
(2.3)

A full study of cluster and layer size, and of theory level effects on the calculated ΔH_{ads} has been conducted using an H-MFI model because the greatest amount of experimental data was available for the sixteen probe molecules used herein (top 16 molecules in Table 2.1). A QM/QM/MM model that was deemed accurate for H-MFI was then applied to H-BEA and H-FAU zeolite frameworks in order to study how changing the pore size and shape affected binding enthalpies [72-75]. In order to investigate transferability across different frameworks and because full sets of experimental ΔH_{ads} for the sixteen probe molecules were not available, we also investigated the binding of a number of alkanes (see Table 2.1) in H-MFI, H-BEA and H-FAU and compared with experimental data, when available.

The calculations involving quantum layers are subject to the basis set superposition error (BSSE). There is no exact way to correct for BSSE in ONIOM calculations. The most obvious way for both two- and three-layer ONIOM models is to isolate the QM layer (capped with H atoms to saturate the dangling bonds) and perform a counterpoise correction on it and the substrate molecule; we follow this approach here as well [61, 63, 65, 66]. The adsorption schemes are summarized in eqns. 2.4 and 2.5.

$$\Delta H_{ads}(2 \text{ layer}) = [H(H,SL) + H(L,RL) - H(L,SL)]_{z+ads} + BSSE(H,SL)_{z+ads} - [H(H,SL) + H(L,RL) - H(L,SL)]_z - H(H)_{ads}$$
(2.4)

$$\Delta H_{ads}(3 \text{ layer}) = [H(H,SL) + H(M,IL) + H(L,RL) - H(M,SL) - H(L,IL)]_{Z+ads} +BSSE(H,SL)_{Z+ads} - [H(H,SL) + H(M,IL) + H(L,RL) - H(M,SL) - H(L,IL)]_{Z} - H(H)_{ads}$$
(2.5)

Zeolite		H-MFI	H-BEA	H-FAU
	Proton			
Molecule	affinity	$\Delta \mathbf{H}_{\mathrm{ads,Exp.}}$	$\Delta ext{H}_{ ext{ads,Exp.}}$	$\Delta extsf{H}_{ extsf{ads,Exp.}}$
Water ^a	165.0	-21.5 ± 2.4		
<i>Benzene^a</i>	179.3	-15.5 ± 1.2		
<i>Methanol^a</i>	180.3	-27.5 ± 1.2		
Ammonia ^a	204.0	-34.7 ± 1.2		
2-Fluoropyridine ^a	211.8	-32.3 ± 3.1		
<i>Methylamine^a</i>	214.1	-44.2 ± 1.2		
3-Fluoropyridine ^a	214.8	-45.4 ± 1.7		
3-Chloropyridine ^a	215.7	-45.4 ± 2.2		
<i>Ethylamine</i> ^a	218.0	-46.6 ± 1.2		
n-Butylamine ^a	219.0	-52.6 ± 1.2		
Dimethylamine ^a	220.5	-49.0 ± 1.2		
<i>Isopropylamine^a</i>	220.8	-49.0 ± 1.2		
<i>Pyridine</i> ^a	222.0	-47.8 ± 1.2		
3-Methylpyridine ^a	222.8	-53.8 ± 2.4		
2-Methylpyridine ^a	223.7	-58.6 ± 2.2		
<i>Trimethylamine^a</i>	226.8	-49.0 ± 1.2		
<i>Methane^b</i>	129.9			
<i>Ethane^b</i>	142.5			
$Propane^{b}$	149.5	-10.8		-7.4
<i>n-Butane^b</i>		-14.2		-9.4
n-Pentane ^b		-17.1		-11.0
n -Hexan e^b		-20.4	-15.3	-12.7
n-Heptane ^b		-22.5		-16.4
n-Octane ^b		-25.4		
^a Microcalorimetry at 32.	3-480K [84-88] ^k	Average of IR and	calorimetry experi	ments at 300-650K

Table 2.1. Experimental adsorbate proton affinities and enthalpies of adsorption (kcal mol⁻¹).

[72-75]

In those cases where the most stable adsorbed state is the one with the acidic proton on the adsorbate, the counterpoise corrections were performed on the protonated adsorbate and the zeolite conjugate base [90].

2.3 Results

2.3.1 Quantum cluster and two-layer ONIOM

In Table 2.2, we present binding enthalpies in H-MFI, modeled with a 17T quantum cluster and two two-layer ONIOM clusters, 17T:120T and 17T:209T. For the 17T cluster, the calculations are performed at the M06-2X/6-31G(d,p) and M06-2X/6-311G(2df,p) theory levels; the ONIOM calculations are performed at the M06-2X/6-31G(d,p):UFF and M06-2X/6-311G(2df,p):UFF levels.

By the mean signed error (MSE) of 6.7 kcal mol⁻¹ and the mean unsigned error (MUE) of 8.1 kcal mol⁻¹, we can see that the 17T quantum cluster under-binds almost systematically when we do not correct for the BSSE. Both the MSE and MUE for BSSE-corrected enthalpies increase to 11 kcal mol⁻¹, indicating that, for the 17T quantum cluster, M06-2X/6-31G(d,p) under-binds systematically. This poor performance does not seem to be basis set related, as increasing the basis set size from 6-31G(d,p) to 6-311G(2df,p) increases the average BSSE-corrected error by 0.5 kcal mol⁻¹. The shortcomings of small or medium-size cluster calculations of adsorption enthalpies are of course well known and here are presented mainly for comparison purposes. Small and medium-sized quantum clusters have been quite reliable for the calculation of activation energies of reactions in zeolites, primarily because the long-range interactions.

Table 2.2. ΔH_{ads} of probe molecules on a 17T quantum cluster and in two-layer embedded cluster ONIOM models of H-MFI. The BSSE-uncorrected enthalpies are shown in parentheses. The 17T quantum calculations are at the M06-2X/6-31G(d,p) and M06-2X/6-311G(2df,p) theory levels. The ONIOM calculations are presented for 17T:120T and 17T:209T mechanically embedded clusters at the M06-2X/6-31G(d,p):UFF and M06-2X/6-311G(2df,p):UFF theory levels. (kcal mol⁻¹)

Small layer theory		M06-2X	M06-2X	M06-2X		M06-2X	
Real laver		/ 6-31G(d,p)	/ 6-311G(2df,p)	/ 6-31G(d,p)		/ 6-311G(2df,p)	
tetrahedral atoms	Exp.	None	None	120T	209T	120T	209T
Water	-21.5	-20.9 (-27.4)	-19.0 (-24.9)	-20.9 (-27.2)	-21.0 (-27.3)	-19.8 (-25.2)	-19.9 (-25.3)
Benzene	-15.5	-6.1 (-10.9)	-7.5 (-10.0)	-12.1 (-16.2)	-13.0 (-17.0)	-13.5 (-15.8)	-14.4 (-16.6)
Methanol	-27.5	-23.7 (-30.0)	-21.8 (-26.7)	-26.8 (-33.0)	-26.9 (-33.2)	-25.8 (-30.6)	-26.0 (-30.8)
Ammonia	-34.7	-35.5 (-37.7)	-32.7 (-34.0)	-31.0 (-33.4)	-31.1 (-33.5)	-29.3 (-30.7)	-29.2 (-30.6)
2-Fluoropyridine	-32.3	-20.5 (-26.1)	-21.4 (-24.7)	-30.4 (-35.1)	-31.1 (-35.8)	-31.3 (-34.5)	-32.1 (-35.2)
Methylamine	-44.2	-39.6 (-42.3)	-38.1 (-39.6)	-38.6 (-41.5)	-39.4 (-42.3)	-38.0 (-39.9)	-38.3 (-40.2)
3-Fluoropyridine	-45.4	-26.3 (-30.7)	-26.9 (-29.2)	-33.2 (-38.0)	-34.1 (-39.0)	-34.0 (-37.2)	-34.8 (-37.9)
3-Chloropyridine	-45.4	-25.3 (-29.1)	-26.1 (-28.5)	-36.6 (-40.1)	-37.7 (-41.1)	-38.1 (-40.6)	-38.4 (-40.8)
Ethylamine	-46.6	-41.7 (-45.1)	-40.0 (-41.8)	-44.3 (-47.9)	-45.0 (-48.6)	-43.8 (-45.9)	-44.1 (-46.2)
n-Butylamine	-52.6	-41.9 (-47.6)	-40.8 (-43.7)	-50.6 (-55.3)	-51.1 (-55.7)	-49.9 (-52.5)	-50.7 (-53.3)
Dimethylamine	-49.0	-41.0 (-44.5)	-40.4 (-42.3)	-43.9 (-47.5)	-44.3 (-47.8)	-44.1 (-46.2)	-44.4 (-46.6)
Isopropylamine	-49.0	-41.9 (-46.0)	-40.3 (-42.5)	-47.0 (-50.5)	-47.4 (-51.0)	-46.1 (-48.2)	-46.7 (-48.8)
Pyridine	-47.8	-31.5 (-35.3)	-31.9 (-34.1)	-35.9 (-40.0)	-36.7 (-40.7)	-37.2 (-39.7)	-37.9 (-40.4)
3-Methylpyridine	-53.8	-31.0 (-35.0)	-31.9 (-34.1)	-42.9 (-46.4)	-43.7 (-47.2)	-43.9 (-46.2)	-45.0 (-47.3)
2-Methylpyridine	-58.6	-32.0 (-36.2)	-32.8 (-35.4)	-45.2 (-49.0)	-46.1 (-50.0)	-45.6 (-48.2)	-46.5 (-49.1)
Trimethylamine	-49.0	-37.2 (-41.5)	-37.1 (-39.4)	-35.4 (-39.8)	-36.1 (-40.5)	-36.2 (-38.8)	-36.4 (-39.0)
Mean signed error		11.0 (6.7)	11.5 (8.9)	6.1 (2.0)	5.5 (1.4)	6.0 (3.3)	5.5 (2.8)
Mean unsigned error		11.1 (8.1)	11.5 (9.3)	6.1 (4.5)	5.5 (4.3)	6.0 (4.5)	5.5 (4.3)

Calculations of interactions and confinement phenomena remain an issue when we calculate adsorption enthalpies, because similar error cancellation does not occur.

The two-layer models M06-2X/6-31G(d,p):UFF and M06-2X/6-311G(2df,p):UFF show a marked improvement (Table 2.2). The incorporation of the third, fourth, and fifth tetrahedral UFF coordination spheres around the Al atom improves the BSSE-corrected MUE to 6.1 and 6.0 kcal mol-1 for the 6-31G(d,p) and 6-311G(2df,p) small layers basis sets, respectively, but we still see systematic underbinding, despite the fact that the UFF is known to overestimate the van der Waals interactions. It is notable that, when we do not include BSSE corrections, the MUE is lower, 4.5 kcal mol⁻¹ for both the 6-31G(d,p) and 6-311G(2df,p) small layers basis sets (Table 2.2). That notwithstanding, there is clear improvement over the 17T cluster which is most evident in the adsorbates with the larger proton affinities, which bind more strongly in the two-layer ONIOM model – even though the binding enthalpies are still underestimated. Adsorbates with larger proton affinities are able to accept the proton from the zeolite and the resulting ion pair seems to be stabilized through interactions with the pore.

Increasing the size of the real layer to also include the sixth tetrahedral coordination sphere reduces the BSSE-corrected MSE and MUE by *ca.* 0.5 kcal mol⁻¹ both in the case of M06-2X/6-31G(d,p):UFF and in the case of M06-2X/6-311G(2df,p):UFF (Table 2.2). Overall, we see that by extending the size of the real layer (*i.e.*, by including more of the framework) we have additional stabilization of the adsorbed stated on account of attractive van der Waals interactions between the substrate molecule and the walls of the zeolite. However, both ONIOM2 models

investigated here tend to under-bind on average, a behavior that becomes more pronounced and more systematic when we correct for the BSSE.

2.3.2 Three-layer ONIOM – method, basis set and layer size effects

In the following we present results for a number of three-layer QM/QM/MM ONIOM models using a combination of theories and basis sets with a mechanically embedded 17T:23T:97T cluster model of H-MFI. The 17T:23T:97T cluster is of the same size as the 17T:120T cluster used in the ONIOM2 calculations but with 23T atoms of the real layer reassigned to an intermediate quantum layer. In all the models considered, the small layer (17T) is treated at the M06-2X/6-311G(2df,p) level. For the intermediate layer (23T), we assess HF theory and the three functionals B3LYP, M06-2X and ω B97x-D, and the basis sets 3-21G, 6-31G, 6-31G(d,p) and 6-31G(2df,p). The outer layer is modelled with the UFF.

At the ILT/3-21G, ILT/6-31G and ILT/6-311G (ILT = HF, B3LYP, M06-2X, ω B97x-D) levels, we see a dramatic change compared to the ONIOM2 calculations as all four models now over-bind (negative MSE) with MUE in the range 5-10.5 kcal mol⁻¹, without BSSE corrections (Tables 2.3 and 2.4). M06-2X and ω B97x-D over-bind systematically and, in fact, we see an increase in the MUE and in the degree of overbinding as we move from the minimal basis set 3-21G (MUE *ca.* 8.0 kcal mol⁻¹) to 6-31G (MUE *ca.* 10 kcal mol⁻¹). For the 6-311G basis set, however, the MUE drops to the 3-21G level – which is still significantly high and almost twice as large as in the ONIOM2 calculations. For the same basis sets, HF and B3LYP appear better balanced, with MUE in the range 5–6 kcal mol⁻¹. Correcting for the BSSE is more beneficial to M06-2X and ω B97x-D than to HF and B3LYP. For example, the MUE at the M06-2X/6-311G and ω B97x-D/6-311G intermediate levels drops by 2 kcal mol⁻¹ (to 5.5 and 6.2 kcal mol⁻¹, respectively) when we correct for the BSSE. At the HF/6-311G and B3LYP/6-311G intermediate levels, the MUE drops by 0.4 kcal mol⁻¹ (to 4.9 and 5.1 kcal mol⁻¹, respectively) when we correct for the BSSE. Interestingly, when one considers the BSSE-corrected MUE, all four models appear quite equivalent.

The rather large fluctuations in the MUE with the intermediate layer basis sets 3-21G, 6-31G and 6-311G have led us to investigate the effect of adding polarization (Tables 2.5 and 2.6). Specifically, we have performed single-point energy calculations with the intermediate layer basis sets 6-31G(d,p) and 6-31G(2df,p) on geometries optimized at the M06-2X/6-311G(2df,p):ILT/3-21G:UFF and M06-2X/6-311G(2df,p):ILT/6-31G:UFF (ILT = HF, B3LYP, M06-2X, ωB97x-D). For M06-2X and ω B97x-D, the MUE reaches a plateau value of *ca*. 4 kcal mol⁻¹, irrespective of the optimization geometry on which the single-point calculations were performed (Tables 2.5 and 2.6; see also Figures 2.3a and b). Further, correcting for the BSSE leaves the MUE practically unaffected. In contrast, the MUE for HF and B3LYP in the intermediate layer are largely unconverged with respect to the basis set (Figure 2.3). Adding polarization seems less beneficial, as the MUE rises to ca. 9 kcal mol⁻¹ accompanied by significant under-binding, with MSE of ca. 6 kcal mol⁻¹ without BSSE correction and ca. 9 kcal mol⁻¹ with BSSE correction. Clearly, due their intrinsic shortcomings and despite the attendant computational savings, neither HF nor B3LYP are suitable for three-layer QM/QM/MM ONIOM calculations of binding enthalpies; the dispersive interactions between the substrate molecule and the framework surrounding the active site play a significant role.

Table 2.3. ΔH_{ads} of probe molecules in three-layer embedded cluster ONIOM models of H-MFI. The BSSE-uncorrected enthalpies are shown in parentheses. Binding enthalpies of probe molecules in a mechanically embedded 17T:23T:97 H-MFI cluster at the M06-2X/6-311G(2df,p):ILT/3-21G:UFF (ILT = HF, B3LYP, M06-2X, ω B97x-D) ONIOM theory levels. (kcal mol⁻¹)

Small layer theory		M06-2X / 6-311G(2df,p)							
Intermediate layer theory	Exp.	HF / 3-21G	B3LYP / 3-21G	M06-2X / 3-21G	ω B97x-D / 3-21 G				
Water	-21.5	-24.6 (-30.4)	-25.3 (-31.2)	-26.4 (-32.3)	-26.0 (-31.9)				
Benzene	-15.5	-7.7 (-9.8)	-8.8 (-10.9)	-15.5 (-17.8)	-16.0 (-18.1)				
Methanol	-27.5	-28.2 (-33.1)	-29.4 (-34.3)	-31.3 (-36.2)	-31.0 (-35.9)				
Ammonia	-34.7	-39.4 (-40.6)	-40.3 (-41.5)	-42.0 (-43.2)	-41.6 (-42.8)				
2-Fluoropyridine	-32.3	-35.4 (-38.0)	-36.5 (-39.1)	-40.9 (-43.6)	-42.5 (-45.2)				
Methylamine	-44.2	-48.9 (-50.3)	-50.2 (-51.6)	-52.4 (-53.8)	-52.7 (-54.1)				
3-Fluoropyridine	-45.4	-40.9 (-43.4)	-42.4 (-44.9)	-46.8 (-49.3)	-48.5 (-50.9)				
3-Chloropyridine	-45.4	-42.7 (-44.9)	-43.3 (-45.6)	-47.0 (-49.2)	-49.3 (-51.5)				
Ethylamine	-46.6	-53.9 (-55.4)	-55.4 (-56.9)	-58.1 (-59.6)	-59.1 (-60.6)				
n-Butylamine	-52.6	-60.0 (-62.3)	-62.6 (-64.7)	-67.1 (-69.1)	-68.4 (-70.4)				
Dimethylamine	-49.0	-53.6 (-55.4)	-55.2 (-57.0)	-56.9 (-58.7)	-58.3 (-60.0)				
Isopropylamine	-49.0	-57.9 (-59.7)	-60.2 (-61.9)	-63.9 (-65.6)	-65.3 (-67.1)				
Pyridine	-47.8	-43.4 (-45.5)	-44.4 (-46.4)	-48.9 (-51.0)	-50.0 (-52.0)				
3-Methylpyridine	-53.8	-49.7 (-51.8)	-50.7 (-52.8)	-54.5 (-56.6)	-56.8 (-58.9)				
2-Methylpyridine	-58.6	-49.9 (-52.1)	-50.7 (-52.9)	-53.5 (-55.8)	-55.5 (-57.8)				
Trimethylamine	-49.0	-45.1 (-47.4)	-47.1 (-49.2)	-53.5 (-55.7)	-53.0 (-55.0)				
Mean signed error		-0.5 (-2.9)	-1.8 (-4.2)	-5.4 (-7.8)	-6.3 (-8.7)				
Mean unsigned error		5.0 (5.5)	5.4 (5.9)	6.0 (8.1)	6.7 (8.8)				

Table 2.4. Dependence of ΔH_{ads} on intermediate layer basis set in H-MFI. The BSSE-uncorrected enthalpies are shown in parentheses. Binding enthalpies of probe molecules in a mechanically embedded 17T:23T:97 H-MFI cluster at the M06-2X/6-311G(2df,p):ILT/6-31G:UFF (ILT = HF, B3LYP, M06-2X, ω B97x-D) ONIOM theory levels. (kcal mol⁻¹)

Small layer theory		M06-2X / 6-3	811G(2df,p)						
Intermediate layer theory	Exp.	HF / 6-31G	B3LYP / 6-31G	M06-2X / 6-31G	ωB97x-D / 6-31G	HF / 6-311G	B3LYP / 6-311G	M06-2X / 6-311G	ωB97x-D / 6-311G
Water	-21.5	-25.2 (-31.0)	-25.5 (-31.3)	-27.1 (-32.9)	-26.9 (-32.7)	-23.9 (-29.6)	-24.2 (-30.0)	-25.9 (-31.7)	-25.5 (-31.3)
Benzene	-15.5	-6.4 (-8.5)	-7.0 (-9.1)	-13.1 (-15.3)	-14.6 (-16.6)	-4.6 (-6.8)	-5.0 (-7.2)	-11.6 (-13.8)	-12.9 (-15.0)
Methanol	-27.5	-28.6 (-33.5)	-28.9 (-33.8)	-31.5 (-36.4)	-32.0 (-36.9)	-26.7 (-31.5)	-27.1 (-32.0)	-30.0 (-34.9)	-30.1 (-35.0)
Ammonia	-34.7	-41.6 (-42.8)	-42.0 (-43.2)	-44.0 (-45.1)	-44.3 (-45.5)	-39.0 (-40.2)	-40.0 (-41.2)	-42.0 (-43.2)	-42.0 (-43.2)
2-Fluoropyridine	-32.3	-37.4 (-39.9)	-37.6 (-40.2)	-42.7 (-45.4)	-44.8 (-47.4)	-34.4 (-37.0)	-35.2 (-37.8)	-40.7 (-43.3)	-42.3 (-44.9)
Methylamine	-44.2	-51.0 (-52.3)	-51.5 (-52.8)	-54.3 (-55.7)	-55.1 (-56.4)	-48.0 (-49.3)	-48.9 (-50.2)	-51.9 (-53.3)	-52.5 (-53.8)
3-Fluoropyridine	-45.4	-41.9 (-44.4)	-42.5 (-44.9)	-47.7 (-50.2)	-49.8 (-52.2)	-39.0 (-41.4)	-40.0 (-42.3)	-45.6 (-47.9)	-47.0 (-49.4)
3-Chloropyridine	-45.4	-44.8 (-47.0)	-45.0 (-47.1)	-49.3 (-51.5)	-51.5 (-53.7)	-42.2 (-44.4)	-42.7 (-44.9)	-47.3 (-49.5)	-49.4 (-51.5)
Ethylamine	-46.6	-56.3 (-57.9)	-56.5 (-58.0)	-60.1 (-61.8)	-61.7 (-63.2)	-53.2 (-54.7)	-53.8 (-55.3)	-57.4 (-59.1)	-58.6 (-60.1)
n-Butylamine	-52.6	-60.7 (-62.9)	-61.2 (-63.3)	-67.2 (-69.2)	-69.1 (-71.0)	-57.7 (-59.9)	-58.7 (-60.8)	-64.5 (-66.5)	-66.1 (-68.1)
Dimethylamine	-49.0	-55.9 (-57.7)	-56.2 (-58.0)	-59.3 (-61.2)	-60.9 (-62.7)	-52.6 (-54.4)	-53.5 (-55.3)	-56.7 (-58.5)	-58.1 (-59.9)
Isopropylamine	-49.0	-58.6 (-60.4)	-59.2 (-61.0)	-64.4 (-66.2)	-66.3 (-68.0)	-55.2 (-57.0)	-56.3 (-58.1)	-61.9 (-63.6)	-63.4 (-65.2)
Pyridine	-47.8	-45.7 (-47.7)	-45.8 (-47.8)	-51.0 (-53.1)	-52.4 (-54.5)	-42.6 (-44.6)	-43.2 (-45.3)	-49.2 (-51.2)	-50.1 (-52.1)
3-Methylpyridine	-53.8	-52.3 (-54.4)	-52.4 (-54.5)	-57.1 (-59.1)	-59.4 (-61.5)	-48.9 (-50.9)	-49.7 (-51.7)	-54.7 (-56.7)	-56.8 (-58.8)
2-Methylpyridine	-58.6	-53.1 (-55.2)	-53.5 (-55.6)	-56.9 (-59.2)	-59.0 (-61.3)	-50.3 (-52.4)	-51.2 (-53.4)	-54.9 (-57.2)	-56.9 (-59.1)
Trimethylamine	-49.0	-47.2 (-49.5)	-47.2 (-49.3)	-55.3 (-57.3)	-55.8 (-57.8)	-43.6 (-45.9)	-43.4 (-45.6)	-52.0 (-54.1)	-52.1 (-54.2)
Mean signed error		-2.1 (-4.5)	-2.4 (-4.8)	-6.8 (-9.2)	-8.2 (-10.5)	0.7 (-1.7)	0.0 (-2.4)	-4.6 (-7.0)	-5.7 (-8.0)
Mean unsigned error		5.1 (5.9)	5.2 (6.0)	7.3 (9.2)	8.3 (10.5)	4.9 (5.3)	5.1 (5.5)	5.5 (7.4)	6.2 (8.1)

Table 2.5. Effect of intermediate layer basis set polarization on ΔH_{ads} in H-MFI. The BSSE-uncorrected enthalpies are shown in parentheses. Binding enthalpies of probe molecules in a mechanically embedded 17T:23T:97 H-MFI cluster at the M06-2X/6-311G(2df,p):ILT/6-31G(d,p) (BS1):UFF//M06-2X/6-311G(2df,p):ILT/3-21G:UFF and at the M06-2X/6-311G(2df,p):ILT/6-31G(2df,p) (BS2):UFF//M06-2X/6-311G(2df,p):ILT/3-21G:UFF ONIOM theory levels, where ILT = HF (T1), B3LYP (T2), M06-2X (T3), ω B97x-D (T4). (kcal mol⁻¹)

Small layer theory		M06-2X / 6-311G(2df,p)							
Intermediate layer theory	Exp.	T1/BS1 // T1/3-21G	T2/BS1 // T2/3-21G	T3/BS1 // T3/3-21G	T4/BS1 // T4/3-21G	T1/BS2 // T1/3-21G	T2/BS2 // T2/3-21G	T3/BS2 // T3/3-21G	T4/BS2 // T4/3-21G
Water	-21.5	-20.4 (-26.3)	-20.9 (-26.8)	-21.9 (-27.8)	-22.1 (-28.0)	-19.4 (-25.3)	-19.8 (-25.7)	-20.7 (-26.6)	-21.0 (-26.9)
Benzene	-15.5	-4.0 (-6.1)	-4.4 (-6.5)	-9.0 (-11.3)	-12.6 (-14.7)	-3.5 (-5.6)	-3.8 (-5.9)	-8.2 (-10.5)	-12.2 (-14.2)
Methanol	-27.5	-21.5 (-26.4)	-22.3 (-27.2)	-24.5 (-29.4)	-24.7 (-29.6)	-20.0 (-24.9)	-20.8 (-25.7)	-22.9 (-27.8)	-23.2 (-28.1)
Ammonia	-34.7	-33.1 (-34.4)	-33.8 (-35.0)	-35.2 (-36.4)	-35.4 (-36.7)	-31.0 (-32.2)	-31.7 (-32.9)	-32.9 (-34.1)	-33.3 (-34.5)
2-Fluoropyridine	-32.3	-28.4 (-31.0)	-29.4 (-32.0)	-33.8 (-36.5)	-36.1 (-38.8)	-26.2 (-28.9)	-27.4 (-30.0)	-31.7 (-34.4)	-34.1 (-36.8)
Methylamine	-44.2	-41.3 (-42.7)	-42.3 (-43.7)	-44.6 (-46.0)	-45.6 (-47.0)	-38.9 (-40.3)	-39.9 (-41.3)	-42.2 (-43.6)	-43.2 (-44.6)
3-Fluoropyridine	-45.4	-32.4 (-34.9)	-33.3 (-35.8)	-37.8 (-40.3)	-40.1 (-42.6)	-30.3 (-32.8)	-31.5 (-33.9)	-35.8 (-38.3)	-38.2 (-40.7)
3-Chloropyridine	-45.4	-37.0 (-39.2)	-37.7 (-39.9)	-41.8 (-44.1)	-44.4 (-46.6)	-35.0 (-37.3)	-36.0 (-38.2)	-40.1 (-42.3)	-42.7 (-44.9)
Ethylamine	-46.6	-46.1 (-47.6)	-47.1 (-48.6)	-49.8 (-51.3)	-51.5 (-53.0)	-43.5 (-45.0)	-44.6 (-46.1)	-47.3 (-48.8)	-49.0 (-50.5)
n-Butylamine	-52.6	-49.6 (-51.8)	-51.3 (-53.5)	-56.3 (-58.3)	-58.4 (-60.3)	-46.9 (-49.1)	-48.7 (-50.9)	-53.7 (-55.6)	-55.8 (-57.8)
Dimethylamine	-49.0	-46.1 (-47.8)	-47.1 (-48.8)	-49.7 (-51.4)	-51.6 (-53.3)	-43.6 (-45.4)	-44.8 (-46.5)	-47.3 (-49.0)	-49.3 (-51.0)
Isopropylamine	-49.0	-47.8 (-49.6)	-49.7 (-51.4)	-54.4 (-56.1)	-56.4 (-58.2)	-45.3 (-47.1)	-47.3 (-49.0)	-52.0 (-53.7)	-54.0 (-55.8)
Pyridine	-47.8	-36.7 (-38.8)	-37.5 (-39.5)	-42.1 (-44.1)	-43.7 (-45.7)	-34.5 (-36.6)	-35.4 (-37.4)	-39.9 (-41.9)	-41.6 (-43.7)
3-Methylpyridine	-53.8	-42.9 (-45.0)	-43.5 (-45.6)	-48.0 (-50.1)	-50.7 (-52.8)	-40.6 (-42.7)	-41.4 (-43.5)	-45.8 (-47.9)	-48.7 (-50.7)
2-Methylpyridine	-58.6	-45.2 (-47.4)	-45.9 (-48.1)	-49.2 (-51.5)	-51.6 (-53.9)	-43.3 (-45.4)	-44.2 (-46.4)	-47.4 (-49.7)	-50.0 (-52.3)
Trimethylamine	-49.0	-37.2 (-39.5)	-37.7 (-39.9)	-43.5 (-45.6)	-45.3 (-47.4)	-35.0 (-37.3)	-35.4 (-37.6)	-40.5 (-42.7)	-43.0 (-45.1)
Mean signed error		6.4 (4.0)	5.6 (3.2)	2.0 (-0.4)	0.2 (-2.2)	8.5 (6.1)	7.5 (5.1)	4.0 (1.6)	2.1 (-0.3)
Mean unsigned error		6.4 (4.8)	5.7 (4.5)	3.9 (4.0)	3.6 (3.8)	8.5 (6.5)	7.5 (5.6)	4.6 (3.8)	3.7 (3.3)

Table 2.6. Effect of intermediate layer basis set polarization on ΔH_{ads} in H-MFI. The BSSE-uncorrected enthalpies are shown in parentheses. Binding enthalpies of probe molecules in a mechanically embedded 17T:23T:97 H-MFI cluster at the M06-2X/6-311G(2df,p):ILT/6-31G(d,p) (BS1):UFF//M06-2X/6-311G(2df,p):ILT/6-31G:UFF and at the M06-2X/6-311G(2df,p):ILT/6-31G(2df,p) (BS2):UFF//M06-2X/6-311G(2df,p):ILT/6-31G:UFF ONIOM theory levels, where ILT = HF (T1), B3LYP (T2), M06-2X (T3), ω B97x-D (T4). (kcal mol⁻¹)

Small layer theory		M06-2X / 6-3	11G(2df,p)						
Intermediate layer theory	Exp.	T1/BS1 // T1/6-31G	T2/BS1 // T2/6-31G	T3/BS1 // T3/6-31G	T4/BS1 // T4/6-31G	T1/BS2 // T1/6-31G	T2/BS2 // T2/6-31G	T3/BS2 // T3/6-31G	T4/BS2 // T4/6-31G
Water	-21.5	-20.7 (-26.5)	-21.4 (-27.2)	-22.5 (-28.3)	-22.5 (-28.3)	-19.6 (-25.4)	-20.2 (-26.1)	-21.3 (-27.1)	-21.3 (-27.2)
Benzene	-15.5	-4.1 (-6.2)	-5.1 (-7.2)	-9.9 (-12.2)	-12.7 (-14.8)	-3.7 (-5.8)	-4.6 (-6.7)	-9.2 (-11.5)	-12.3 (-14.4)
Methanol	-27.5	-22.1 (-27.0)	-23.0 (-27.9)	-25.1 (-30.0)	-25.7 (-30.6)	-20.5 (-25.4)	-21.4 (-26.3)	-23.6 (-28.4)	-24.1 (-29.0)
Ammonia	-34.7	-33.4 (-34.6)	-34.2 (-35.4)	-35.6 (-36.8)	-35.9 (-37.1)	-31.3 (-32.4)	-32.1 (-33.3)	-33.3 (-34.5)	-33.7 (-34.9)
2-Fluoropyridine	-32.3	-29.0 (-31.5)	-30.1 (-32.7)	-34.7 (-37.3)	-37.0 (-39.6)	-26.9 (-29.5)	-28.3 (-30.8)	-32.7 (-35.4)	-35.1 (-37.7)
Methylamine	-44.2	-41.9 (-43.2)	-43.2 (-44.5)	-45.4 (-46.7)	-46.2 (-47.5)	-39.4 (-40.7)	-40.9 (-42.2)	-42.9 (-44.3)	-43.8 (-45.1)
3-Fluoropyridine	-45.4	-33.5 (-35.9)	-35.1 (-37.5)	-39.8 (-42.3)	-41.8 (-44.2)	-31.6 (-34.0)	-33.4 (-35.8)	-38.1 (-40.5)	-40.0 (-42.4)
3-Chloropyridine	-45.4	-37.1 (-39.2)	-37.8 (-40.0)	-41.9 (-44.1)	-44.0 (-46.2)	-35.0 (-37.2)	-36.1 (-38.2)	-40.1 (-42.3)	-42.2 (-44.4)
Ethylamine	-46.6	-46.9 (-48.5)	-47.9 (-49.5)	-50.7 (-52.4)	-52.5 (-54.0)	-44.3 (-45.8)	-45.5 (-47.0)	-48.2 (-49.9)	-50.0 (-51.5)
n-Butylamine	-52.6	-50.7 (-52.9)	-52.1 (-54.3)	-57.5 (-59.5)	-59.4 (-61.4)	-48.1 (-50.3)	-49.5 (-51.7)	-54.9 (-56.9)	-56.9 (-58.8)
Dimethylamine	-49.0	-46.6 (-48.4)	-47.5 (-49.3)	-50.1 (-51.9)	-51.8 (-53.6)	-44.0 (-45.8)	-45.1 (-46.9)	-47.6 (-49.4)	-49.4 (-51.2)
Isopropylamine	-49.0	-48.5 (-50.3)	-50.3 (-52.0)	-55.1 (-56.8)	-57.0 (-58.7)	-46.0 (-47.7)	-47.9 (-49.6)	-52.6 (-54.3)	-54.5 (-56.2)
Pyridine	-47.8	-37.1 (-39.1)	-38.1 (-40.1)	-42.7 (-44.8)	-44.3 (-46.3)	-34.9 (-36.9)	-36.0 (-38.1)	-40.7 (-42.7)	-42.3 (-44.3)
3-Methylpyridine	-53.8	-43.6 (-45.6)	-44.4 (-46.5)	-48.5 (-50.6)	-51.0 (-53.0)	-41.3 (-43.3)	-42.4 (-44.5)	-46.4 (-48.5)	-49.0 (-51.0)
2-Methylpyridine	-58.6	-45.6 (-47.7)	-46.5 (-48.6)	-49.4 (-51.7)	-51.8 (-54.0)	-43.6 (-45.7)	-44.8 (-46.9)	-47.7 (-50.0)	-50.1 (-52.4)
Trimethylamine	-49.0	-37.6 (-39.9)	-37.7 (-39.8)	-44.4 (-46.5)	-45.6 (-47.7)	-35.3 (-37.6)	-35.4 (-37.5)	-41.7 (-43.8)	-43.2 (-45.3)
Mean signed error		5.9 (3.5)	4.9 (2.5)	1.2 (-1.2)	-0.4 (-2.8)	8.0 (5.6)	6.8 (4.5)	3.2 (0.8)	1.6 (-0.8)
Mean unsigned error		5.9 (4.6)	5.2 (4.5)	3.9 (4.1)	3.7 (4.0)	8.0 (6.1)	6.8 (5.1)	4.2 (3.7)	3.6 (3.5)



Figure 2.3. Mean unsigned error at various intermediate layer theories. (a) BSSEuncorrected and (b) BSSE-corrected values.

Of all the probe molecules investigated for this study, pyridine and its chlorofluoro- and methyl-derivatives and the amines posed a great challenge to the two-layer ONIOM methodology. The MSE calculated over the subset of the pyridines and amines is 8.1 and 5.0 kcal mol⁻¹, respectively. In contrast, the three-layer models perform significantly better. For example, at the M06-2X/6-311G(2df,p):M06-2X/6-31(d,p):UFF//M06-2X/6-311G(2df,p):M06-2X/6-31G:UFF level, the MSE dropped to 4.3 and -2.1 kcal mol⁻¹, showing the importance of the intermediate quantum mechanical layer for the binding of basic molecules. The decrease in the error relative to the ONIOM2 models – of the same size – and the almost similar behavior of the intermediate layer theories in the ONIOM3 models suggest the importance of electrostatic interactions and of charge polarization in particular. QM/MM methods with mechanically embedded QM regions do not consider the polarization of the quantum region (*i.e.* of the active site) by the framework and *vice versa*, force fields with fixed partial charges on the atoms do not react to changes in the electron density of the quantum region. QM/MM formulations with electrostatic embedding address the former problem because the Hamiltonian includes an extra term with the electrostatic potential, but they still suffer from the latter, which is of some significance when we calculate transition states, as there is no reason to assume that the polarization of the MM region will not be affected along the reaction pathway. However, by introducing a quantum mechanical intermediate layer which replaces part of the MM layer, we partly ameliorate the lack of polarization; at the same time, we are also treating the dispersion interactions more accurately than with the UFF [91].

We have also investigated the effects of the size of the intermediate and real layers on the binding enthalpy (Table 2.7). We have considered three H-MFI clusters, 17T:23T:97T, 17T:61T:59T and 17T:23T:186, modelled at the M06-2X/6-311G(2df,p):M06-2X/6-31(d,p):UFF//M06-2X/6-311G(2df,p):M06-2X/3-21G:UFF level. In the 17T:61T:59T cluster, we have reassigned 38 atoms of the real layer of 17T:23T:97T to the intermediate layer, while keeping the total number of atoms fixed. In the 17T:23T:186T cluster, we have added atoms within the sixth coordination sphere of 17T:23T:97T. The results are presented in Table 2.7 and in Figure 2.4. The MUE, with or without BSSE corrections, remains practically flat and independent of the size of the cluster, indicating that, overall, it is not affected in any significant way when we extend the MM layer beyond the sixth coordination sphere around the Al atoms of the active site (fluctuating around the value of *ca.* 3.8 kcal mol⁻¹). We have seen similar

Theory		M06-2X/6-311G	(2df,p):M062X/3-	21G:UFF	M06-2X/6-311G(2df,p):M06-2X/6-31G(d,p):UFF // M06-2X/6-311G(2df,p):M062X/3-21G:UFF				
SL:IL:RL tetrahedral atoms	Exp.	17T:23T:97T	17T:61T:59T	17T:23T:186T	17T:23T:97T	17T:61T:59T	17T:23T:186T		
Water	-21.5	-26.4 (-32.3)	-25.9 (-31.8)	-26.5 (-32.4)	-21.9 (-27.8)	-21.3 (-27.2)	-22.0 (-27.9)		
Benzene	-15.5	-15.5 (-17.8)	-18.5 (-20.4)	-16.2 (-18.5)	-9.0 (-11.3)	-11.2 (-13.2)	-9.6 (-11.9)		
Methanol	-27.5	-31.3 (-36.2)	-31.2 (-36.2)	-31.5 (-36.4)	-24.5 (-29.4)	-23.6 (-28.6)	-24.7 (-29.6)		
Ammonia	-34.7	-42.0 (-43.2)	-43.4 (-44.6)	-42.1 (-43.3)	-35.2 (-36.4)	-36.0 (-37.2)	-35.2 (-36.4)		
2-Fluoropyridine	-32.3	-40.9 (-43.6)	-44.6 (-47.4)	-41.7 (-44.3)	-33.8 (-36.5)	-32.3 (-35.1)	-34.5 (-37.2)		
Methylamine	-44.2	-52.4 (-53.8)	-53.7 (-55.0)	-52.6 (-54.0)	-44.6 (-46.0)	-44.8 (-46.1)	-44.8 (-46.2)		
3-Fluoropyridine	-45.4	-46.8 (-49.3)	-50.8 (-53.2)	-47.5 (-50.0)	-37.8 (-40.3)	-37.4 (-39.9)	-38.5 (-41.0)		
3-Chloropyridine	-45.4	-47.0 (-49.2)	-50.9 (-53.1)	-48.0 (-50.2)	-41.8 (-44.1)	-40.6 (-42.8)	-42.7 (-44.9)		
Ethylamine	-46.6	-58.1 (-59.6)	-60.2 (-61.6)	-58.5 (-60.0)	-49.8 (-51.3)	-49.0 (-50.4)	-50.1 (-51.6)		
n-Butylamine	-52.6	-67.1 (-69.1)	-67.6 (-69.4)	-67.9 (-69.9)	-56.3 (-58.3)	-52.0 (-53.8)	-57.0 (-59.0)		
Dimethylamine	-49.0	-56.9 (-58.7)	-59.1 (-60.8)	-57.3 (-59.0)	-49.7 (-51.4)	-49.7 (-51.4)	-49.9 (-51.7)		
Isopropylamine	-49.0	-63.9 (-65.6)	-64.8 (-66.4)	-64.5 (-66.2)	-54.4 (-56.1)	-52.8 (-54.4)	-55.0 (-56.7)		
Pyridine	-47.8	-48.9 (-51.0)	-52.7 (-54.6)	-49.6 (-51.7)	-42.1 (-44.1)	-40.8 (-42.7)	-42.7 (-44.7)		
3-Methylpyridine	-53.8	-54.5 (-56.6)	-58.7 (-60.9)	-55.5 (-57.5)	-48.0 (-50.1)	-47.2 (-49.3)	-48.8 (-50.9)		
2-Methylpyridine	-58.6	-53.5 (-55.8)	-58.3 (-60.7)	-54.5 (-56.8)	-49.2 (-51.5)	-48.3 (-50.7)	-50.1 (-52.4)		
Trimethylamine	-49.0	-53.5 (-55.7)	-55.8 (-57.9)	-54.0 (-56.2)	-43.5 (-45.6)	-42.6 (-44.7)	-43.9 (-46.1)		
Mean signed error		-5.4 (-7.8)	-7.7 (-10.1)	-5.9 (-8.3)	2.0 (-0.4)	2.7 (0.3)	1.5 (-0.9)		
Mean unsigned error		6.0 (8.1)	7.7 (10.1)	6.4 (8.6)	3.9 (4.0)	3.8 (3.7)	3.8 (3.9)		

Table 2.7. Dependence of ΔH_{ads} on intermediate	layer and real layer sizes in	H-MFI. The BSSE-uncorrected enthalpies	are
shown in parentheses. (kcal mol ⁻¹)			

behavior in the two-layer ONIOM models presented earlier. Extending the intermediate layer can lead to minor improvement.

2.3.3 Adsorption of alkanes in H-MFI, H-BEA and H-FAU

To test transferability, we have extended our calculations to include frameworks of different pore sizes, specifically H-BEA and H-FAU. Experimentally determined adsorption enthalpies for the series of 16 adsorbates investigated above were not available for H-BEA and H-FAU. Numerous studies have, however, investigated the adsorption of linear alkanes in H-MFI, H-BEA and H-FAU. Measurement of their adsorption enthalpies is not without issues, as the acidic zeolite environments cause alkanes to rapidly undergo isomerization, alkylation, and other reactions, and thereby the average of these experimental adsorption enthalpies has been taken as a best estimate for the real system [72-75]. In Table 2.8, we present calculations with and without polarization in the intermediate layer using a 17T:23T:97T cluster for H-MFI, a 16T:18T:77T cluster of H-BEA and a 14T:16T:188T cluster for H-FAU.

Two trends are observed, both in the experimental and computational results. First, as the alkane chain length increases, the adsorption strength increases. When comparing the adsorption strengths with increasing alkane chain length for a given zeolite system, the slope of the computational and experimental results are similar, suggesting that the model does capture this effect. Adding polarization to the intermediate layers in this model was very important, as can be seen in the case of H-MFI. Without polarization H-MFI has a MUE of 9.6 kcal mol⁻¹, which decreases to 5.8 and 5.3 kcal mol⁻¹ for the 6-31G(d,p) and 6-311G(2df,p) basis sets. In the case of H-BEA, the MUE is equal to 3.1 kcal mol⁻¹, while in H-FAU the MUE is 1.7 kcal mol⁻¹. In the case of H-MFI, the error is somewhat larger than in the other two zeolites because



Figure 2.4. Behavior of mean unsigned error with intermediate and real layer sizes and intermediate layer theory.

of the smallest pore and the higher proximity of the adsorbate to the wall of the pore, which is treated with the UFF. As the pore size increases, the adsorbate does not interact as much with the UFF layer, and the error decreases. Nonetheless, the accuracy is quite satisfactory in all three cases, especially if one considers the uncertainty in the experimental enthalpies of adsorption.

Second, as the average pore size of the zeolite decreases, the adsorption strength of a given alkane increases, in qualitative agreement with the expectation for these zeolite systems [72-75]. It is well established that binding enthalpy increases (in absolute value) as the pore size decreases and becomes more confining. For these three

Table 2.8. ΔH_{ads} for <i>n</i> -alkanes in H-MFI, H-BEA and H-FAU. The BSSE-uncorrected enthalpies are shown in parentheses.
The sizes of the embedded clusters are as indicated. The enthalpies are calculated at the M06-2X/6-311G(2df,p):
M06-2X/6-31G(d,p):UFF//M06-2X/6-311G(2df,p):M062X/3-21G:UFF ONIOM level. (kcal mol ⁻¹)

Zeolite	H-MFI	H-BEA	H-FAU	H-MFI	H-BEA	H-FAU	H-MFI	H-BEA	H-FAU	H-MFI	H-BEA	H-FAU
SL:IL:RL T-atoms				17T:23T :97T	16T:18T :77T	14T:16T :188T	17T:23T :97T	16T:18T :77T	14T:16T :188T	17T:23T :97T	16T:18T :77T	14T:16T :188T
Theory		Exp. ^a		Theory 1*			Theory 2*	*		Theory 3*	**	
Methane	[-5.3]	[-2.7]	[-2.9]	-8.8 (-9.6) -13.4	-6.5 (-7.4)	-5.5 (-6.1)	-7.3 (-8.2)	-5.9 (-6.8) -8 3	-4.0 (-4.6) -8.1	-7.0 (-7.8) -11.6	-5.8 (-6.7) -8.1	-3.7 (-4.3)
Ethane	[-8.2]	[-5.2]	[-5.0]	(-14.6) -20.0	(-10.3) -13.9	(-9.8) -10.5	(-13.2) -17.3	(-9.5) -13.2	(-9.5) -8.9	(-12.9) -16.8	(-9.4) -13.0	(-9.4) -8.6
Propane	-10.8	[-7.8]	-7.4	(-21.5) -23.8	(-15.2) -15.7	(-12.0) -12.5	(-18.8) -20.4	(-14.4) -14.9	(-10.4) -10.9	(-18.3) -19.9	(-14.3) -14.8	(-10.1) -10.4
n-Butane	-14.2	[-10.3]	-9.4	(-25.5) -28.1	(-17.5) -18.6	(-14.3) -15.6	(-22.1) -23.7	(-16.7) -16.9	(-12.6) -13.8	(-21.6) -23.1	(-16.7) -16.7	(-12.1) -13.2
n-Pentane	-17.1	[-12.8]	-11.0	(-29.6) -32.7	(-19.8) -18.0	(-17.6) -18.8	(-25.3) -27.0	(-18.1) -15.8	(-15.8) -16.1	(-24.7) -26.4	(-17.9) -15.5	(-15.2) -15.4
n-Hexane	-20.4	-15.3	-12.7	(-34.4) -35.4	(-19.8) -23.5	(-20.8) -21.7	(-28.7) -30.0	(-17.6) -21.4	(-18.1) -18.5	(-28.1) -29.2	(-17.3) -21.0	(-17.5) -17.8
n-Heptane	-22.5	[-17.8]	-16.4	(-37.2) -38.9	(-25.1) -25.9	(-23.7) -23.2	(-31.8) -32.7	(-23.0) -22.4	(-20.6) -20.0	(-31.0) -32.1	(-22.6) -22.0	(-19.9) -19.2
n-Octane	-25.4	[-20.3]	[-17.8]	(-40.6)	(-27.5)	(-25.3)	(-34.5)	(-24.0)	(-22.1)	(-33.8)	(-23.6)	(-21.3)
Mean signed error Mean unsigned				-9.6 (-11.1)	-4.9 (-6.3)	-4.2 (-5.9)	-5.8 (-7.3)	-3.3 (-4.8)	-2.2 (-3.9)	-5.3 (-6.8)	-3.1 (-4.5)	-1.7 (-3.4)
error				9.0 (11.1)	4.9 (6.3)	4.2 (5.9)	5.8 (7.3)	3.3 (4.8)	(3.9)	5.5 (6.8)	(4.5)	(3.4)

^a Values in brackets are projected based on a linear fit of the remaining alkane values ^{*} Theory 1 - M06-2X/6-311G(2df,p):M062X/3-21G:UFF; ^{**} Theory 2 - M06-2X/6-311G(2df,p):M06-2X/6-31G(d,p):UFF // M06-2X/6-311G(2df,p):M062X/3-21G:UFF; ^{***} Theory 3 - M06-2X/6-311G(2df,p):M06-2X/6-311G(2df,p):UFF // M06-2X/6-311G(2df,p):M062X/3-21G:UFF

frameworks, the pore size varies in the order H-FAU > H-BEA > H-MFI, [76] and thereby, the relative binding would be expected to follow the order H-FAU < H-BEA < H-MFI.

2.3.4 Relationship between proton affinity and the enthalpy of adsorption

By making use of thermodynamic cycles, differences in the binding strengths of probe molecules in Brønsted acidic zeolites have been correlated with differences in the proton affinities (PA) of the probe molecules themselves. The thermodynamic cycle involves a state in which the acidic proton has been donated to the substrate molecule (see Figure 2.5 inset). The result of this assumption is a linear correlation of unit slope between ΔH_{ads} and the PA. For any given zeolite, this is not a strong correlation, because not all substrate molecules are strong enough bases to accept the acidic proton. Thus, while the correlation might be useful in assessing relative binding strengths of strong bases or of a strong base and of a weak one, the PA of the adsorbate is not a reliable descriptor of the relative binding strength of molecules with weak basicity [68, 86, 87, 92-94].

Adsorbates with gas phase PA greater than *ca.* 200 kcal mol⁻¹ demonstrate the ability to abstract the proton from the zeolite and form an ion pair structure. In this range, the thermodynamic cycle holds and we see that both the experimental and computational data sets correlate well where the model predicts adsorption strengths which linearly coorelate to gas phase PA's with unit slope [86, 87, 92-94]. In this range of PA, the quantum intermediate layer has contributed to the electrostatic stabilization of the ion pair. At low PA of less than *ca.* 180 kcal mol⁻¹, the adsorbate is unable to abstract the proton of the active site and binding is primarily affected through dispersion and hydrogen bonding interactions in the pore. The thermodynamic cycle no longer



Figure 2.5. Correlation between gas phase proton affinity and ΔH_{ads} in H-MFI zeolites. Calculations performed using the 17T:61T:59T model of H-MFI at the M06-2X/6-311G(2df,p):M06-2X/6-31G(d,p):UFF // M06-2X/6-311G(2df,p):M06-2X/3-21G:UFF theory level with BSSE correction. In the catalytic cycle, DPE_z is the deprotonation energy of the zeolite, PA_A is the gas phase proton affinity of the adsorbate, and ΔH_{Z-AH} is the interaction energy between the deprotonated zeolite and the protonated adsorbate. Dotted lines show second order fits of the experimental and computational data to guide the eye when compared to the blue line, showing the predicted binding strength using the gas phase proton affinity (PA) correlation with a slope of 1 [86, 87, 92-94].

holds, and we see that both experimental and computational models deviate from the predicted linear trend of unit slope [86, 87, 92-94]. In these cases, the use of a theory in the intermediate layer able to account for dispersion forces between the adsorbate and zeolite walls (M06-2X and ω B97x-D), as well as the benefit of adding polarization to the basis set to allow directional interaction between the adsorbate and pore wall can be seen in the accuracy of these models.

2.4 Discussion

Although detailed quantitative comparisons with experiment can at times prove quite challenging, as the experimental values are a statistical average over a distribution of acid sites, adsorbate-site geometries, and adsorbate configurations whereas the calculated values refer to optimized binding geometries at a particular acid site and adsorbate configuration, comparisons between different computational strategies can prove quite instructive. The handling of long-ranged electrostatic interactions by embedded cluster QM/MM strategies has been a source of concern to critics of this methodology. Below, we compare our results with published periodic-DFT calculations and find very good agreement, which should allay some of the reservations about hybrid QM/MM calculations.

For the adsorption of *n*-C3 to *n*-C6 alkanes at the T12 site of the zigzag channel of H-ZSM-5, Tranca *et al* [95]. have reported binding energies of -11.5, -15.1, -19.1 and -22.0 kcal mol⁻¹, respectively, using periodic-DFT calculations at the PBE-D theory level. At the same theory level, Chiu *et al* [96]. have more recently reported binding energies of -16.3, -19.9, -21.8 and -24.9 kcal mol⁻¹, respectively, which are very close to those calculated by us (-16.8, -19.9, -23.1 and -26.4 kcal mol⁻¹, respectively) with a 17T:23T:97T three-layer ONIOM model at the M06-2X/6-311G(2df,p):M06-2X/6-311G(2df,p):UFF//M06-2X/6-311G(2df,p):M062X/3-21G:UFF (Table 2.8). Chiu *et al.* have also calculated binding energies with the semilocal exchange-correlation functional vdW-DF2, which is designed to take into account dispersion interactions in a non-empirical way [51]. The reported values of -16.0, -20.8, -23.2 and -28.2 kcal mol⁻¹, respectively, are very close to PBE-D, and to those calculated by us.

Chiu *et al.* have also reported binding energies of water and methanol in H-ZSM-5 using periodic-DFT. For water, the PBE-D value of -22.2 kcal mol⁻¹ fares very well upon comparison with the experimental value of -21.5 kcal mol⁻¹ and is close to our value of -21.3 kcal mol⁻¹. On the other hand, the vdW-DF2 value of -17.2 kcal mol⁻¹ ¹ somewhat underestimates water adsorption. For methanol, the PBE-D value of -24.4 is close to our value of -23.6 kcal mol⁻¹, whereas the vdW-DF2 functional somewhat underestimates binding, predicting an energy of -21.3 kcal mol⁻¹.

Even though more systematic benchmarking is required to fully access strengths and weaknesses in the performance of QM/QM/MM embedded cluster ONIOM models for predicting adsorption in zeolites, they do not seem to under-perform relative to periodic-DFT calculations.

In Table A.1 of Appendix A, we show the calculated adsorption entropies of *n*-C1 to *n*-C8 alkanes in H-MFI, assuming a molecular surface area of 200×600 (pm × pm) [97] for 2-dimensional free translations of the guest molecule. In the temperature range of 25 to 200 °C, the computed values vary little with temperature. Upon comparison with experimental values reported by De Moor *et al.* for *n*-C3 to *n*-C6 alkanes [97], the computed values systematically overestimate the entropic losses, but they are, nevertheless, in good agreement with experiment, with an error of no more than 10 J mol⁻¹ K⁻¹. Despite the good agreement with experiment, we are of the opinion that the entropic error that is associated with the notoriously inaccurate low-frequencies in the harmonic approximation cannot be fully addressed by the qRRHO approximation. Sauer and co-workers [98-100], in recent work that was inspired by earlier work by Njegic and Gordon [101], have convincingly argued and demonstrated that correcting for the error in the adsorption entropy due to the soft modes requires not only consideration of the strong anharmonic character of these modes, but also that the diagonalization of the Hessian be performed in the curvilinear space of the intrinsic

coordinates of the system. This approach is not entirely without problems, as it is not always easy to find appropriate intrinsic coordinates, nor is it entirely computationally inexpensive for large systems (factor of 10 computational overhead) [100] as the anaharmonicity calculation requires a number of single-point energy calculations to sample the potential energy surface along a normal mode in curvilinear space.

2.5 Conclusions

We have explored mechanically embedded three-layer QM/QM/MM ONIOM models for computational studies of binding in metal-substituted zeolites. In all the models considered, the high-level-theory layer consists of the adsorbate molecule and of the framework atoms within the first two coordination spheres of the metal atom and is treated at the M06-2X/6-311G(2df,p) level. For simplicity and flexibility in partitioning the system into QM and MM regions in a number of ways without worrying about the net charge of the MM region not being zero, the outer, low-level-theory layer is treated with the UFF. We have modelled the intermediate-level layer quantum mechanically and investigated the performance of HF theory and of three DFT functionals, B3LYP, M06-2X and ω B97x-D, for different layer sizes and various basis sets, with and without BSSE corrections. We have studied the binding of sixteen probe molecules with a broad range of basicities in H-MFI and compared the computed adsorption enthalpies with published experimental data. We have demonstrated that HF and B3LYP are inadequate for the description of the interactions between the probe molecules and the framework surrounding the metal site of the zeolite, on account of being unable to capture dispersion forces. Both M06-2X and ω B97x-D on average converge within ca. 10% of the experimental values, at the M06-2X/6-
311G(2df,p):M06-2X/6-31G(d,p):UFF//M06-2X/6-311G(2df,p):M06-2X/3-21:UFF

ωB97x-D/6-311G(2df,p):ωB97x-D/6-31G(d,p):UFF and // ωB97x-D/6-311G(2df,p):ωB97x-D/3-21:UFF theory levels, respectively. In particular, the threelayer ONIOM models perform significantly better than the two-layer model M06-2X/6-311G(2df,p):UFF in stabilizing ion-pair structures of adsorbate molecules with high proton affinities. The mean errors over the subsets of the pyridines and of the amines drop significantly showing the importance of the intermediate quantum mechanical layer for the stabilization of ion-pairs. We have further computed the binding enthalpies of n-alkanes (C1-C8) in H-MFI, H-BEA and H-FAU at the M06-2X/6-311G(2df,p):M06-2X/6-31G(d,p):UFF // M06-2X/6-311G(2df,p):M06-2X/3-21:UFF theory level and found very good agreement with experiment, with mean unsigned errors of 5.3, 3.1 and 1.7 kcal mol⁻¹, respectively, demonstrating transferability of the model across zeolite frameworks and classes of molecules. The transferability is further demonstrated by the good agreement between computed entropies of adsorption and experimental values reported by De Moor *et al.* for the adsorption of *n*-C3 to *n*-C6 alkanes in H-ZSM-5.

2.6 Acknowledgements

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Chapter 3

KINETIC REGIME CHANGE IN THE TANDEM DEHYDRATIVE AROMATIZATION OF FURAN DIELS-ALDER PRODUCTS

3.1 Introduction

Research into the production of biorenewable fuels and chemicals has rapidly expanded in the past decade in an effort to reduce dependence on traditional, nonrenewable resources [4, 102]. Coinciding with the increased research effort into biomass-derived fuels and chemicals, shale gas production has also greatly expanded in the United States. This newly tapped energy source has the potential to provide vast quantities of C_1 and C_2 hydrocarbons but lacks the ability to provide larger olefins and aromatic chemicals [103]. Within this framework, utilization of biomass-derived sugars has the potential to provide the chemical industry with a more feedstock-diverse source of C_{4+} and aromatic chemicals that is close to carbon-neutral [104-108].

One major biorenewable chemical of interest is *p*-xylene, which may be produced from biomass-derived 2,5-dimethylfuran (DMF) and ethylene. DMF can be produced from glucose via hydroxymethylfurfural [109, 110], and ethylene can be obtained from dehydration of biomass-derived ethanol [22, 111]. Diels–Alder [4 + 2] cycloaddition of DMF and ethylene has been shown to form an oxanorbornene cycloadduct in a single elementary step, after which multistep dehydration forms *p*xylene and water [26, 27]. Renewable *p*-xylene has been proposed as a source for the production of terephthalic acid, which is used in the manufacture of plastic bottles, clothing, automobile components, and many other products [9, 29]. Efforts to maximize the production of *p*-xylene from DMF have demonstrated 90% *p*-xylene yield over H-BEA zeolite in heptane solvent [21]. Heptane has proven effective at greatly reducing competing side reactions, such as alkylation of *p*-xylene with ethylene, formation of polymers from aromatics and furans, and hydrolysis of the furan by the water produced in the dehydrative aromatization (Figure 3.1) [26, 112].

Despite a high yield of *p*-xylene formation from dimethylfuran, the role of the active catalytic site of H-Y zeolites and associated kinetics remains to be understood. The rate at which *p*-xylene is produced with a H-Y (Si/Al 2.6-40) zeolite catalyst has been reported to be independent of the number of available Brønsted acid sites [19], and thus, it was inferred that the rate-limiting step should be *uncatalyzed*. However, in a different study of the reaction of DMF and ethylene with WO_x-ZrO₂ catalyst, the rate of formation of *p*-xylene was instead reported as having linear dependence on the density of acid sites [20]. Quantum chemical calculations have shown that Brønsted acids do not significantly catalyze the Diels-Alder reaction between furans and ethylene [26, 27, 113]. Acidic protons have a higher affinity for the furan than ethylene and, in particular, for the ring carbons of the furan – where the HOMO amplitude is the largest – which breaks the requisite orbital symmetry for [4 + 2] cycloaddition [26, 27, 114]. However, the second reaction, dehydration of the Diels-Alder cycloadduct of DMF and ethylene, cannot proceed uncatalyzed; Brønsted acids reduce the kinetic energy barrier by as much as 45 kcal/mol and are essential for this step [26, 27, 113].

Variation in the dependence of the rate of p-xylene formation on the type and concentration of Brønsted acids thus raises intriguing questions about the kinetics of the reaction (cycloadduct formation and subsequent dehydration to p-xylene, as shown in Figure 3.1) and more generally about the kinetics of tandem reactions, which, in



Figure 3.1. Reactions in the production of p-Xylene from DMF and ethylene.

conjunction with bifunctional catalysts can be utilized in the design of efficient, one-pot synthetic processes. In this study, we present kinetic data that show that the concentration of Brønsted acid sites gives rise to two distinct kinetic regimes in the tandem scheme of Diels-Alder cycloaddition and dehydrative aromatization to *p*xylene. Using hybrid quantum mechanics/molecular mechanics (QM/MM) calculations and microkinetic modeling, we show that in the first kinetic regime, in which the overall rate of *p*-xylene formation grows linearly with the density of acid sites, the kinetics are controlled by the *catalyzed* dehydration of the Diels-Alder cycloadduct. In contrast, in the second regime, in which the rate is independent of the density of acid sites, the kinetic bottleneck is the *uncatalyzed* Diels-Alder reaction. At high catalyst loadings, there are enough free active sites to catalyze dehydration, and as a result, the homogeneous Diels-Alder reaction becomes rate-limiting, consistent with the fact that this is the most energetically demanding step of the mechanism. The linear regime occurs at low catalyst loadings, and because there are not enough active sites to catalyze it, the dehydrative aromatization reaction becomes rate-controlling, despite the fact that it requires a lower activation energy than the cycloaddition reaction. Finally, we present a reduced kinetic model to show that the two regimes are characteristic of tandem schemes in which the first reaction proceeds uncatalyzed while the second reaction is catalyzed.

3.2 Methods

3.2.1 Experiment

Experiments examined the kinetics of the reaction of DMF and ethylene with faujasite catalysts within gas/liquid/solid reactors.

3.2.1.1 Reaction setup

Reactions were performed in Parr 4560 series reactors equipped with 4848 controllers and gas entrainment impellers to eliminate mass transport limitations. Chemicals were used without further purification and consisted of 2,5-dimethylfuran (Alfa Aesar 98+%), *n*-heptane (Alfa Aesar 99+%), ethylene gas (Airgas UHP), and *n*-tridecane (Sigma-Aldrich 98+%) as an internal standard. An H-Y faujasite catalyst with a Si/Al ratio of 2.6 (Zeolyst CBV 600) was used for all of the reactions and dried in a furnace at 200 °C prior to use. Reaction procedure involved loading the vessel with DMF, heptane, tridecane, and catalyst prior to heating and initiation of the reaction by adding 200 psi of ethylene gas and maintaining pressure throughout the course of the experiment. Additionally, the second Damköhler number was estimated to be equal to

 $0.0002 \ll 0.1$, which indicates the absence of mass transfer limitations between gaseous and solution phase ethylene (Figure B.1). The reaction rate was found to be independent of particle size, which implies that intraparticle diffusion is not rate limiting either.

3.2.1.2 Reaction orders and activation energies

Dependence of reaction rate on catalyst loading was investigated using 1.38 M DMF in *n*-heptane, with 0.082 M *n*-tridecane as an internal standard and 14 bar (200 psi) ethylene pressure. These initial concentrations and pressures were used as the standard reaction conditions. Experiments investigating the reaction regimes of Figure 3.2 were performed at 200 and 250 °C by varying the catalyst loading from 0.3 to 1.5 g to yield effective Brønsted acid site concentrations between 1.1 and 5.1 mM. Experiments investigating the parameters of reaction rate expressions (i.e., reaction orders) were performed at low and high catalyst loadings (1.3 and 5.1 mM) for both DMF and ethylene at 200 °C. The concentration of DMF in DMF reaction order experiments varied from 0.46 to 2.3 M in 0.46 M increments. In ethylene reaction order experiments, the ethylene pressure varied from 6.9 to 34.5 bar in 6.9 bar increments (100–500 psi in 100 psi increments), yielding ethylene concentrations of 0.036–0.18 M in 0.036 M increments. Ethylene concentrations were estimated from previous measurements [115]. Experiments investigating the activation energies of Figure 3.2 were performed at 0.3 and 1.5 g by varying the temperature from 200 to 250 °C in 10 °C increments using the standard reaction conditions above.



Figure 3.2. Kinetics of *p*-xylene production with H-Y zeolite catalyst: experiment. (A) Rate of *p*-xylene production at 200 and 250 °C relative to strong acid site concentration. (B) Arrhenius plot at 1.3 mM H-Y acid site concentration. (C) *p*-Xylene reaction rate with respect to dimethylfuran (DMF; □) and ethylene (▲) at 1.3 mM H-Y acid site concentration. (D) Arrhenius plot at 1.3 mM H-Y acid site concentration. (E) *p*-Xylene reaction rate with respect to dimethylfuran rate with respect to dimethylfuran rate with respect to dimethylfuran (DMF; □) and ethylene (▲) at 5.1 mM H-Y acid site concentration.

3.2.1.3 Reaction-product characterization

Characterization of chemical components within the reaction mixture was performed with an Agilent 6890 gas chromatograph equipped with a G1513A autosampler, HP-Innowax column (to achieve separation of o,m,p-xylene isomers), and a flame ionization detector. Samples were collected under reaction conditions at high temperature and pressure utilizing a double block sampling system, which allows for samples to be taken without opening the reaction vessel. Major species were identified by matching retention times with pure standards. All reported data exhibited carbon balance closure greater than or equal to 90%.

3.2.2 Computational

Quantum mechanics/molecular mechanics (QM/MM) calculations have been used to calculate the relevant adsorption energies and reaction barriers for the chemistry of interest, using a three-layer, mechanically embedded ONIOM cluster model. The computed energies were then used to parametrize a microkinetic model.

3.2.2.1 QM/MM calculations

The reaction pathway calculations were performed on a HAISi₃₁₃O cluster model (314 tetrahedral atoms) of H-Y. The model was cut out from the periodic structure of pure faujasite zeolite [76], and the dangling bonds were saturated with hydrogen atoms. Three-layer ONIOM models [37, 77, 78] were employed to perform all calculations within the zeolite for the purposes of capturing the local active site and surrounding zeolite pore environments. For reactions within the zeolite, the high layer, comprising the active site and its environment (the active hexagonal ring and the six surrounding 4-T rings, a total of 18 T atoms, HAlSi₁₇O₂₄), was treated quantum mechanically with the M06-2X functional [81]. The adsorbates, the Brønsted H atom, the aluminum atom of the zeolite and the oxygen atoms in its first coordination shell, viz. nearest neighbors, were modeled with the 6-31G(d,p) basis set, while the rest of the high layer zeolite atoms were modeled with the effective core potential basis set LANL2DZ. The medium layer, the supercage in which the reaction takes place, was modeled at the M062X/3-21G level and kept frozen after optimization of the bare zeolite. For the modeling of the low ONIOM layer, the rest of the zeolite cluster, we employed the molecular mechanics force field UFF [116]; the atoms of this layer were kept frozen in their crystallographic positions at all times. The zeolite was optimized in the absence of adsorbates and only the high layer was allowed to relax in the presence of adsorbates. Binding energies are sensitive to the basis set of the quantum mechanical region and susceptible to basis set superposition error. Thus, for the adsorption of reactants, intermediates, and products within the zeolite H-Y, we used a second ONIOM model with a slightly smaller high layer which, however, allowed us to use triple- ζ valence basis functions and additional polarization. In this model consisting of 218 tetrahedral atoms (HAlSi₂₁₇O₃₅₂), the high layer consisted of the 14 T atoms in the first two coordination spheres around the substituted aluminum atom and was modeled at the M062X/6-311G(2df,p) level. The intermediate layer included the 16 T atoms in the third coordination sphere around the substituted aluminum atom and was modeled at the M062X/3-21G level and kept frozen. The remaining 188 T atoms in the fourth through sixth coordination spheres were modeled with the molecular mechanics force field UFF, with atoms being kept frozen in their crystallographic positions. This model was benchmarked against adsorption experimental data (not shown). Solution phase calculations of isolated reactants and products were performed with the SMD model [117] at the M062X/6-311G(2df,p) theory level. All calculations were performed with the Gaussian 09 (Rev. A.2) program [80].

3.2.2.2 Reaction network

The reaction network consists of the following reactions: homogeneous and heterogeneous Diels-Alder cycloaddition of DMF and ethylene; homogeneous and heterogeneous cycloadduct dehydration comprising of three elementary reaction steps; heterogeneous DMF hydrolysis [26, 118]; and adsorption/desorption steps of reactants, products and stable intermediates [26, 27].

3.2.2.3 Reaction rate constants and microkinetic modeling

The calculated free energies of activation and reaction were used to parametrize a microkinetic model, as detailed in Appendix B. Given the uncertainty in QM/MM calculations and especially in the entropic contributions to the free energies of reaction and activation, we introduced a design of experiment (DOE) approach to investigate the sensitivity of multiple, experimentally measured parameters (*p*-xylene production rate, apparent activation energy, and reaction orders) to multiple model parameters (the binding strengths of oxanorbornene, DMF, and hexanedione; the homogeneous Diels-Alder Gibbs free energy of reaction; and the heterogeneous dehydration reaction barrier), which were identified to be important through sensitivity analysis of the microkinetic model. This methodological innovation departs from the traditional singleparameter-change-at-a-time sensitivity analysis and is reminiscent of global sensitivity analysis subject to constraints imposed by our experimental measurements. Details of this approach can be found in Appendix B, and the final set of parameters used to build the microkinetic model can be found in Table B.1. All adjustments to the final parameters were found to be within the expected computational error. A global sensitivity analysis was also performed.

3.3 Results and Discussion

3.3.1 Experimental kinetics of reaction of DMF and ethylene

The rate of *p*-xylene production exhibits complex dependence on the relative concentrations of reactants (DMF and ethylene) and strong acid sites in H-Y zeolite. As shown in Figure 3.2A, the rate of p-xylene production at 200 and 250 $^{\circ}$ C exhibits linear dependence on the concentration of strong Brønsted acid sites at the given conditions

and low acid site concentrations (<3.0 mM). However, above ~3.0 mM acid site concentration, the rate of *p*-xylene formation becomes independent of strong acid site concentration; for these conditions, the addition of more catalyst has no impact on the overall formation rate of *p*-xylene ($r_{p-xylene} \propto [H^+]^Z$, $Z \sim 0$).

Differences in the two regimes of Figure 3.2 extend to the measurable kinetic parameters. As depicted in Figures 3.2B and D, Arrhenius plots generated at low acid site concentration (1.3 mM [H+]) and high acid site concentration (5.1 mM [H⁺]) exhibit statistically different activation energies: low acid concentration conditions lead to an activation energy of 10.8 ± 2.1 kcal/mol, and high acid concentration conditions exhibit an activation energy of 20.1 ± 1.2 kcal/mol. Moreover, the rate of formation of *p*-xylene exhibits variable dependence on the reactant concentrations between the two kinetic regimes, as measured at $200 \,^\circ$ C. At low acid concentration (1.3 mM [H⁺]), the reaction rate expression for *p*-xylene formation has first-order dependence on ethylene (r_{p} -xylene $\propto [C_2H_4]^X$, $X = 1.01 \pm 0.07$) and half-order dependence on dimethylfuran (r_{p} -xylene $\propto [DMF]^Y$, $Y = 0.49 \pm 0.08$), determined from the data of Figure 3.2. However, at high acid concentrations (5.1 mM [H+]), the rate of p-xylene $\propto [C2H4]X[DMF]Y$; $X = 0.90 \pm 0.13$, $Y = 0.79 \pm 0.07$), as determined from the data of Figure 3.2E.

3.3.2 QM/MM calculations of relevant energies and barriers

Calculation of the adsorption of reactants, intermediates, products, and transition states within the zeolite pore environment provides mechanistic understanding of the chemistry at the strong acid site within H-Y. The calculated adsorption strengths from the HAlSi₂₁₇O₃₅₂ ONIOM model can be found in Table B.1 and adsorption geometries are shown in Figure 3.3. Calculations show that among the reactants and products,



Figure 3.3. Adsorption of dimethylfuran, *p*-xylene, oxanorbornene and hexanedione in faujasite. (A) ONIOM model (218T) used for adsorption calculations where atoms represented by balls-and-sticks are in the high layer, tube frames are in the intermediate layer, and wireframes are in the low layer (white, hydrogen; gray, carbon; red, oxygen; pink, aluminum; and green-gray, silicon). Adsorption complexes extracted from the ONIOM model of (B) DMF, (C) *p*-xylene, (D) oxanorbornene, and (E) 2,5-hexanedione are also shown, where the distances from the active site proton to the nearest atom of the adsorbate are provided in units of Å.

DMF (17.9 kcal/mol) and *p*-xylene (16.6 kcal/mol) bind more strongly to the active site than either ethylene (9.0 kcal/mol) or water (11.1 kcal/mol). Examining the DMF and *p*-xylene adsorption geometries on the catalyst surface (Figure 3.3B and 3.3C), we see that both molecules coordinate to the active site with their aromatic carbons atoms. The oxanorbornene intermediate formed by the Diels-Alder cycloaddition reaction of DMF and ethylene strongly adsorbs to the surface of the zeolite (25.8 kcal/mol), with the bridging oxygen atom located closest to the active site (Figure 3.3D). 2,5-Hexanedione, formed by the hydrolysis of DMF with water, also binds strongly (25.9 kcal/mol), with an oxygen from one of the keto groups being closest to the active site (Figure 3.3E).

Tandem Diels-Alder, dehydrative aromatization pathways within Brønsted acidic zeolites have been previously discussed [26, 27, 113]; here, we provide comprehensive energetics of all elementary steps, obtained from ONIOM calculations on the HAlSi₃₁₃O₅₂₀ cluster model (Figure 3.4) and detailed understanding of the dominant reaction pathways via a microkinetic model (MKM). Energies for the uncatalyzed reaction mechanism in Figure 3.4 show that the Diels-Alder reaction has a barrier of 39.5 kcal/mol, and the largest barrier of the subsequent dehydration of the oxanorbornene intermediate is 60.1 kcal/mol. In the calculations from the ONIOM model accounting for catalysis at the H-Y zeolite active site and surrounding pore, the Diels-Alder reaction barrier of dimethylfuran and ethylene remains about the same, with a barrier of 43.4 kcal/mol; however, there is a significant decrease in the largest dehydration reaction barrier to 14.4 kcal/mol. From the depicted reaction barriers of Figure 3.4, it is clear that H-Y does not catalyze the Diels-Alder reaction between DMF and ethylene. Dehydration of the oxanorbornene cycloadduct is, however, orders of magnitude faster in the Brønsted acidic zeolite H-Y. Fast proton transfer from the zeolite active site to the bridging oxygen atom initiates the reaction. The oxanorbornene oxygen bridge, C2-O, breaks with activation energy of only 14.4 kcal/mol, which is 45.7 kcal/mol lower than the uncatalyzed reaction barrier. The binding of the proton to the bridging oxygen appears to stabilize the transition state for the C2-O cleavage, making this reaction much more favorable. In the acid catalyzed case, the slowest step along this pathway is the uncatalyzed Diels-Alder cycloaddition. The furan ring of DMF may open hydrolytically upon β -C protonation and subsequent water addition at the adjacent α-C [118].



Figure 3.4. Free energy profile of *p*-xylene production from DMF and ethylene. Diels-Alder cycloaddition of DMF and ethylene followed by dehydrative aromatization occurs in the absence (dashed line; homogeneous phase) and presence (solid line; heterogeneous phase) of H-Y zeolite. Calculated intermediate and transition states account for the influence of the zeolite pore.

3.3.3 Microkinetic model results and discussion

By the calculated energies of Figure 3.4, one would conclude that Diels-Alder cycloaddition should be the rate-limiting reaction for all acid-catalyzed reactions, a result differing from the experimental results of Figure 3.2, which indicates two distinct kinetic regimes. To probe the kinetics of the acid-catalyzed system, the QM/MM calculations for adsorption energies and reaction barriers were used to develop a microkinetic model (MKM) by the details provided in the Methods section and Table B.1.

Figure 3.5A shows the predicted rate of p-xylene production as a function of acid site concentration from the MKM. The MKM (green line) agrees well with experimental data at 200 and 250 °C. The two kinetic regimes were captured by the

MKM: at low acid site concentrations, the *p*-xylene production rate varies with the acid site concentration, whereas at high acid site concentrations, the *p*-xylene production rate is independent of acid site concentration. In addition, a global sensitivity analysis was performed on the MKM model such that the adsorption strength of oxanorbornene and DMF to the active site, the homogeneous Diels-Alder Gibbs free energy of reaction, and the heterogeneous dehydration reaction barrier provided a confidence interval that indicated that the parametrized model was robust in describing the *p*-xylene production rate. These energies were independently perturbed using a normal distribution with a standard deviation of 1.5 kcal/mol. The 95% confidence interval, depicted as a green region in Figure 3.5A, encompasses the experimental data points at 250 °C.

Figure 3.5B depicts the solution phase concentrations predicted by the MKM with reaction time. Consumption of DMF and formation of *p*-xylene predicted by the model are in agreement with experiments. A consumption rate of DMF slower than expected could be because the model does not include side reactions beyond DMF hydrolysis to hexanedione. Further Diels-Alder reactions between DMF and the cycloadduct or unproductive pathways through the dehydrative aromatization intermediates can also be responsible for loss of DMF, but they are not considered in the current model [112]. Nevertheless, the close agreement between the experimental and model concentration profiles that 2,5-hexanedione makes up the majority of side products present in the reaction. The 2,5-hexanedione that is formed is able to reversibly convert back into DMF to be further converted into *p*-xylene, and therefore, as the conversion of DMF increases, the thermodynamics of the system reduce the presence of 2,5-hexanedione product found in solution and help drive the system to high yields of *p*-xylene.



Figure 3.5. Model comparisons with experimentally available data. (A) *p*-Xylene initial production rate at Brønsted acid concentrations at 250 °C. *p*-Xylene production rates are calculated as the average rate over the first 50 min of reaction time at the specified temperature and catalyst loading. (B) Solution-phase composition experiments (points) and simulations (lines). Conditions: 2.0 g of H-Y (Si/Al = 2.6) for an effective acid site concentration of 6.8 mM, 1.38 M DMF, at 250 °C. MKM results are shown as lines, and experimental data are shown as points. The values in red are the solution phase concentration of 2,5-hexanedione from the model and the sum of all side products from the experimental data.

Analysis of the MKM (Figure 3.6) provides detailed understanding of the active reaction pathways. For both the high (5.1 mM [H⁺], red) and low (0.1 mM [H⁺], blue) catalyst loading scenarios, the reaction pathway to p-xylene is the same. The homogeneous Diels-Alder reaction accounts for 65% of the flux of DMF in solution in a reversible reaction, and the remaining DMF in solution adsorbs on the catalyst surface and undergoes hydrolysis with water to 2,5-hexanedione. It can be seen that the adsorbed DMF does not undergo heterogeneous Diels-Alder reaction, but rather, a hydrolysis reaction. Of the oxanorbornene formed by homogeneous Diels-Alder



Figure 3.6. Abridged reaction network and simulation reaction path fluxes. Diels-Alder and dehydration reactions in homogeneous (green) and heterogeneous (blue) phases and hydrolysis of DMF. Inactive pathways are represented in gray. Fluxes calculated by the MKM model are provided as percentages of the total flux of DMF initially fed into the reactor averaged over the first 50 min. of reaction at 250 °C at Brønsted acid sit concentrations of 0.1 mM (low loading, blue) and 5.1 mM (high loading, red).

reaction, it can be seen that none of it is homogeneously dehydrated into *p*-xylene and water, as a result of the prohibitively high reaction barrier. Rather, all of the oxanorbornene adsorbs on the catalyst surface and undergoes irreversible, heterogeneous dehydration.

With the reaction path analysis revealing the major route for the reaction, uncatalyzed Diels-Alder reaction followed by Brønsted acid catalyzed dehydration, we have examined differences between the two kinetic regimes. Rate-limiting steps for both kinetic regimes have been verified by performing sensitivity analysis of the MKM shown in Figure 3.7. At low acid site concentrations (0.1 mM [H⁺]), the normalized sensitivity coefficients for the heterogeneous dehydration reaction steps (~0.45) are much greater than that of the homogeneous Diels-Alder reaction (0.05), indicating that the heterogeneous dehydration reaction is rate-limiting. In contrast, at high acid site concentrations (5.1 mM [H⁺]), there is a clear shift in the normalized sensitivity



Figure 3.7. Sensitivity analysis of microkinetic model. The normalized sensitivity coefficient is defined as $\ln(r_{pX,Perturbed} - r_{pX,Unperturbed}) /\ln(k_{i,Perturbed} - k_{i,Unperturbed})$. Reaction rate parameters were perturbed by +1% (blue) and -1% (red) at 250 °C for each of the catalyst loadings shown. Dehydration step 1 represents the C-O bond cleavage and dehydration step 2 represents the first proton transfer from the three-step mechanism seen in Figure 3.4.

coefficients (0.62 for the homogeneous Diels–Alder reaction compared with \sim 0.15 for the heterogeneous dehydration reaction), indicating that the homogeneous Diels–Alder reaction is rate-limiting.

Using the MKM, we have determined apparent activation energies and rate orders in the two kinetic regimes, namely, at 0.1, 1.3, and 5.1 mM [H⁺], as shown in Table 3.1 and Figure 3.8A. We should note that although the 1.3 mM active site concentration clearly falls within the experimental linear regime (Figure 3.5A), the same cannot be said of the model. Thus, in the case of the MKM, we have also considered a catalyst loading of 0.1 mM to ensure that we were looking at values well within the model's linear regime and not in a transitional state between the two kinetic regimes.

The differences in the apparent activation energies and reaction orders between the two kinetic regimes are predicted by the MKM and show good agreement with experiment. In the linear kinetic regime, the apparent activation energies (10.8 kcal/mol from experiment and 18.4 kcal/mol from the MKM) are close to the dehydration reaction barrier of 14.5 kcal/mol calculated from the QM/MM calculations. The ~4 kcal/mol difference between the QM/MM calculation and the microkinetic model is due to contributions from the dehydration and hydrolysis reactions included in the model. The DMF reaction order was 0.49 ± 0.08 from experiment and 0.3 from the microkinetic model. At higher catalyst loadings, the apparent reaction barrier increases (20.1 kcal/mol from the QM/MM calculations. In addition, the reaction orders for both DMF and ethylene are close to 1, in support of the homogeneous Diels-Alder reaction mechanism.

The MKM also provides insight into the coverages on the acid sites as a function of conversion (Figure 3.8B). At early times, the high concentration of DMF in solution causes it to occupy the surface of the zeolite. As DMF is converted and forms *p*-xylene, completely cover the surface of the zeolite. The strong adsorption strength of 2,5hexanedione allows it to dominate the surface of the zeolite, despite its lower concentrations in solutions relative to DMF and *p*-xylene (Figure 3.5B). Near complete DMF conversion, however, we see that 2,5-hexanedione is able to reversibly convert back into DMF, driven by the thermodynamics of the system, causing the 2,5hexanedione to desorb. The strong adsorption strength of the oxanorbornene intermediate allows it to compete with 2,5-hexanedione for active sites, enabling the heterogeneous dehydration pathway. The rapid dehydration of the adsorbed

	Experiments		Simulation		
	Low	High	Low	Low	High
	Catalyst	Catalyst	Catalyst	Catalyst	Catalyst
	Loading	Loading	Loading	Loading	Loading
Kinetic Parameter	(1.3 mM)	(5.1 mM)	(0.1 mM)	(1.3 mM)	(5.1 mM)
DMF Reaction					
Order	0.49 ± 0.08	0.79 ± 0.07	0.30 ± 0.02	0.59 ± 0.03	0.73 ± 0.02
Ethylene Reaction					
Order	1.01 ± 0.07	0.90 ± 0.13	0.99 ± 0.00	0.98 ± 0.00	0.98 ± 0.00
Apparent Activation					
Energy [kcal mol ⁻¹]	10.8 ± 2.1	20.1 ± 1.2	18.4 ± 0.2	21.3 ± 0.3	22.7 ± 0.3

Table 3.1. Kinetic parameters for cycloaddition of dimethylfuran and ethylene at different Brønsted acid site concentrations.^a

^a Error bars in simulations are the result of uncertainty quantification.



Figure 3.8. Microkinetic model output. (A) Reaction rate orders as a function of acid site concentration. MKM derived parameters are shown as lines, whereas experimental data is shown as points. (B) Surface coverage of H-Y active sites. Surface coverage of strong acid sites vary as a function of conversion at 250 °C at 5.1 mM of acid site concentration. Coverages do not change significantly when moving from low to high catalyst loading regimes. Oxanorbornene coverage (not shown) is less than 10⁻⁷% at all conversions.

oxanorbornene, however, causes its concentrations on the surface to be very small at all conversions.

3.3.4 Insights into the mechanism

From insights obtained from reaction path and model sensitivity analysis, a simplified kinetic model for the reaction of DMF and ethylene to produce p-xylene consists of the reactions identified in Table 3.2. By this simplified reaction mechanism, the rate of p-xylene production can be solved as

$$\boldsymbol{r_{pX}} = \frac{k_2 K_1 K_4 [DMF][E][H^+]}{K_6 (1+K_3 [W]) [DMF] + \left(\frac{k_2}{k_{-1}}\right) K_4 [H^+]}$$
(3.1)

where k_i and K_i are the reaction rate and equilibrium constants for reaction i, [i] is the concentration of component *i*, and [H⁺] is the total Brønsted acid active site concentration (for details see Appendix B). The functional form of the rate law reveals the presence of two regimes, and its dependence on the concentration of water indicates product inhibition, as water reacts with adsorbed DMF to form 2,5-hexanedione. The reduced model is in good agreement with the microkinetic model; the simplified model is presented as the blue line in Figure 3.5.

At high Brønsted acid active site concentrations, the $[H^+]$ term in the denominator is dominant and the *p*-xylene production rate reduces to,

$$\boldsymbol{r_{pX}} = k_1 [DMF][E] \tag{3.2}$$

The reaction rate depends on the homogeneous Diels-Alder reaction and, therefore, is first-order with respect to DMF and ethylene, in agreement with experiments (Table 3.1). At sufficiently low Brønsted acid active site concentrations, the first term in the denominator is dominant, and the p-xylene production rate instead reduces to

$$\boldsymbol{r_{pX}} = \left(\frac{k_2 K_1 K_4}{K_6 (1 + K_3 [W])}\right) [E] [H^+]$$
(3.3)

No. ^a	Reaction ^b	ki ^c	$\Delta G^{\ddagger_{250^\circ C,i}d}$	k-i	$\Delta G^{\ddagger_{250^\circ C,\text{-}i}d}$
1	$DMF + E \rightleftharpoons CA$	3.5×10 ⁻⁴ M ⁻¹ s ⁻¹	39.5	$1.2 \times 10^3 \text{s}^{-1}$	23.8
	$CA \rightarrow Int1$	8.0×10 ⁻¹³ s ⁻¹	60.1	3.5×10 ⁻¹² s ⁻¹	58.6
	$Int1 \rightarrow Int2$	6.9×10 ⁻⁸ s ⁻¹	48.3	2.0×10 ⁻¹⁰ s ⁻¹	54.4
	$Int2 \rightarrow pX + W$	1.0×10 ⁻⁷ s ⁻¹	47.9	4.9×10 ⁻²⁵ s ⁻¹	89.3
	$DMF * + E \rightleftharpoons CA$	8.1×10 ⁻⁶ M ⁻¹ s ⁻¹	43.4	3.0×10 ⁻⁷ s ⁻¹	46.8
2	$CA * \rightarrow pX + W *$	$1.1 \times 10^7 \text{ s}^{-1}$	14.4	1.1×10 ⁻⁵ M ⁻¹ s ⁻¹	43.1
	$CA * \rightarrow Int1 *$	1.1×10 ⁷ s ⁻¹	14.4	8.9×10 ⁷ s ⁻¹	12.2
	$Int1 * \rightarrow Int2 *$	9.4×10 ⁷ s ⁻¹	12.1	$1.5 \times 10^{1} \text{ s}^{-1}$	28.4
	$Int2 * \rightarrow pX + W *$	3.4×10 ⁸ s ⁻¹	10.8	1.1×10 ⁻⁵ M ⁻¹ s ⁻¹	43.1
3	$DMF * + W \rightleftharpoons HDI *$	2.7×10 ⁵ M ⁻¹ s ⁻¹	18.2	1.3×10 ⁴ s ⁻¹	21.3
No.	Adsorption/Desorption ^b	Ki	$\Delta G_{ads,250^\circ C}{}^d$		
4	$CA + * \rightleftharpoons CA *$	5.84	-1.8		
5	$W + * \rightleftharpoons W *$	0.08	2.6		
6	$DMF + * \rightleftharpoons DMF *$	35.1	-3.7		
7	$HDI + * \rightleftharpoons HDI *$	793	-6.9		
	$E + * \rightleftharpoons E *$	0.05	3.0		
	$pX + * \rightleftharpoons pX *$	0.17	1.9		
	$Hept + * \rightleftharpoons Hept *$	0.003	6.0		
~					_

Table 3.2. Simulated reactions and kinetic parameters.

^aElementary steps with a number are used to derive the reduced model where the numbers correspond to the kinetic parameters found in Equations 1-3. Elementary steps without a number are used in the full microkinetic model.; ^bMolecules are labeled as follows: 2,5-Dimethylfuran (DMF), Ethylene (E), Cycloadduct (CA), p-Xylene (pX), Water (W), 2,5-Hexanedione (HDI), Heptane (Hept), Vacant Acid Site (*); ^cSubscript "i" implies forward reaction while "-i" implies reverse reaction.; ^dReaction barriers and adsorption energies are tabulated in units of kcal mol⁻¹.

The rate has a linear dependence on the Brønsted acid active site concentration, consistent with the findings in the linear regime. In addition, the concentration of DMF appears in both the numerator and the denominator of the rate, and the concentration of ethylene appears only in the numerator. The reduced model supports the variable reaction-order kinetics with respect to DMF (from zero to one) and first-order kinetics with respect to ethylene observed experimentally. The reduced model also supports the experimental trends (Figure 3.5) and indicates that two regimes is a signature of tandem reactions, specifically of a noncatalyzed reaction followed by a heterogeneously catalyzed second reaction.

3.4 Conclusions

We have experimentally and computationally studied the kinetics of formation of *p*-xylene by dehydrative aromatization of the Diels-Alder product between 2,5dimethylfuran and ethylene over H-Y faujasite. This reaction is an archetype of tandem reactions. Cycloaddition proceeds uncatalyzed in solution with a moderate reaction barrier, and dehydration takes place on the active Brønsted acid sites of the zeolite with a low reaction energy barrier. We have shown that two different kinetic regimes exist dependent upon the reactor loading in H-Y faujasite. At high catalyst loadings, there are enough free active sites to catalyze the dehydration reaction, and as a result, the homogeneous Diels-Alder reaction becomes rate-limiting, consistent with the fact that this is the most energetically demanding step of the mechanism. As the catalyst loading decreases past a critical transition value, the kinetics enters the linear regime where, as a result of an insufficient number of active sites, the dehydrative aromatization becomes rate-limiting, despite the fact that it requires less activation than the cycloaddition reaction.

As we noted in the Introduction, in a study of the same reaction by Wang *et al.*, the rate of formation of *p*-xylene was reported as having a dependence on the density of acid sites. This was explained by an alternative mechanism for the formation of the oxanorbornene derivative that did not involve Diels-Alder cycloaddition [20]. This finding was at odds with the kinetic studies of Williams *et al.*, who reported that the rate of *p*-xylene production over H-Y was independent of the density of active sites [19]. We believe that the two kinetic regimes reported and analyzed here can reconcile these two seemingly opposing views. In Williams *et al.*, the reaction was carried out at 300 °C, with an effective catalyst loading range of 1.7–3.2 mM, which is in the flat, cycloaddition-limited regime and, thus, independent of catalyst loading. On the other

hand, in Wang *et al.*, the experiments were performed at 250 °C and significantly lower loadings, ~ 0.2 mM of effective acid site concentration, which lies in the dehydration-limited regime and which explains the reported dependence of the rate on the density of active sites.

Although available acid sites and site acidity may influence the rate of change of the rate of the reaction with acid concentration in the dehydration regime (the slope of the curve in Figure 3.5A), the plateau should remain unaffected because it is determined by the uncatalyzed cycloaddition reaction rate. Thus, the cycloadditionlimited regime should be "universal" to all (Brønsted acid) catalysts. Given that the maximum rate is controlled by the cycloaddition reaction, a logical next step to optimize the process is to develop methods to accelerate the Diels-Alder reaction.

3.5 Acknowledgements

This material has been adapted with permission from Patet, R.E., Nikbin, N., Williams, C.L., Green, S.K., Chang, C.-C., Fan, W., Caratzoulas, S., Dauenhauer, P.J., and Vlachos, D.G. Kinetic regime change in the tandem dehydrative aromatization of furan Diels-Alder products. *ACS Catal.* **2015**, *5*, 2367-2375, Copyright 2015 American Chemical Society. I would like to thank the co-authors of this work, Dr. C. Luke Williams, Dr. Sara K. Green, Dr. Chun-Chih Chang, Prof. Wei Fan, and Prof. Paul J. Dauenhauer for their contribution of materials therein related to experimental synthesis, characterization, and reactions. I would like the co-authors of this work, Dr. Nima Nikbin, Dr. Stavros Caratzoulas and Prof. Dionisios G. Vlachos, for their contributions and insights related to the computational calculations and overall message of the manuscript.

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Chapter 4

GENERAL ACID-TYPE CATALYSIS IN THE DEHYDRATIVE AROMATIZATION OF FURANS TO AROMATICS IN H-[AL]-BEA, H-[FE]-BEA, H-[GA]-BEA, AND H-[B]-BEA ZEOLITES

4.1 Introduction

Aromatic hydrocarbons are high-volume industrial chemicals that are important for the production of a large range of consumer products from plastics to foams, primarily produced through the upgrading of the naphtha portion of crude oil using acidic catalysts [12, 105, 119-122]. Biomass is a feedstock with the potential to reduce the dependence on fossil fuels for the production of aromatics, using furanic platform chemicals, themselves produced from the cellulose and hemicellulose portions of plants [4, 102, 105, 123-125]. Furans can be converted to aromatics through tandem reactions involving the dehydrative aromatization of the Diels-Alder (DA) product of furan and ethylene (Figure 4.1) [19-21, 26, 27, 112, 113, 126]. Experimental and computational studies have shown that Brønsted-acidic catalysts, such as zeolites, are beneficial to this tandem scheme, as they lower the dehydration reaction barrier [26, 27, 113, 126].

This method for the production of aromatics is very effective for the conversion of 2,5-dimethylfuran (DMF) and ethylene to *p*-xylene, with yields of *ca*. 70% for H-BEA zeolite in a heptane solvent [21, 127]. However, the yields of benzene or toluene from furan or 2-methylfuran (MF), respectively, are much lower because of side



Figure 4.1. Reaction scheme for the conversion of furan and ethylene to aromatics.

reactions that lead to catalyst coking and deactivation (*e.g.* Figure 4.2(a)) [19-21, 26, 112, 113, 126, 128]. One side reaction of interest is the acid-catalyzed hydrolysis of furans to ring-opened ketones or aldehydes [113, 118, 126]. The hydrolysis itself is reversible, but in the cases of furan and MF, the products contain formyl and keto groups that can oligomerize or polymerize irreversibly leading, for example, to the trimer-like compound **4** shown in Figure 4.2(b) [112, 129]. These larger polymerization byproducts are difficult to characterize or quantify experimentally using gas chromatography/mass spectrometry (GC/MS) techniques, as they have high boiling points and become trapped in the zeolite pores.

Both the dehydration of the DA cycloaddition product of DMF and ethylene and the hydrolysis of DMF are known to be Brønsted-acid-catalyzed reactions [19, 26, 27, 118, 126, 128]. In a computational study of the H-Y-catalyzed production of *p*-xylene from DMF and ethylene, we showed that the uncatalyzed DA reaction and dehydration



Figure 4.2. (a) Byproducts in the reaction of DMF and ethylene and (b) unique "methylfuran trimer" identified from the reaction of 2-methylfuran and ethylene.

of the resulting cycloadduct have intrinsic free energy barriers of *ca*. 40 and 75 kcal/mol, respectively [126]. The addition of the Brønsted-acidic H-Y catalyst lowered the dehydration reaction barrier to 14 kcal/ mol while providing no catalytic advantage to the DA reaction [126]. Nikbin et al. showed that, in aqueous acidic media, the hydrolysis of DMF follows general acid catalysis with an estimated activation energy of 20-25 kcal/mol [118].

Numerous studies have investigated changing the Brønsted acid strength of zeolite catalysts by exchanging the Al substituent atom by another trivalent metal, for example, B, Ga, or Fe [113, 130-135]. Experimental and computational measurements of adsorption strengths, FTIR frequencies, and chemical reactivities in these solid acid zeolites have attempted to compare their acid strengths, with a predicted trend of [B] < [Fe] < [Ga] < [Al] [135]. These intrinsic measures of acid strength do not always translate into differences in catalytic activity, however. For example, Parrillo et al. demonstrated that HZSM-5 zeolites containing framework Al, Ga, and Fe have very similar heats of adsorption for ammonia and pyridine [136]. When these same materials were used in the reactions of n-hexane cracking and propene oligomerization, however,

H-[Al]- and H-[Ga]-ZSM-5 had similar activities, whereas H-[Fe]-ZSM-5 was less active [136].

A number of experimental and computational studies examining the reactivities of zeolites substituted with boron, the weakest Brønsted acid in the given series, are consistent with the expected low activity [113, 131, 137]. In experimental studies by Kofke et al., H-[B]-ZSM-5 did not catalyze the dehydration of 2-propanol, whereas H-[Al]- and H-[Fe]-ZSM-5 did [131]. This difference was attributed to the weak interactions of reactants in H-[B]-ZSM-5, as measured by temperature-programmed desorption (TPD) [131]. Similarly, in an experimental study, Jones et al. found that the methanol etherification activity was 2 orders of magnitude lower on H-[B]-ZSM-5 than on H- [Fe]-, H-[Ga]-, or H-[Al]-ZSM-5 [137]. In a computational study of *p*-xylene production from DMF and ethylene, Li et al. predicted that H-[B]-BEA would be similarly unreactive as a catalyst because of a larger apparent barrier for the DA reaction, resulting in a decrease in activity of 2 orders of magnitude as compared to that of H-[Ga]- or H-[Al]-BEA [113].

Although that computational study predicted that H-[B]- BEA should be inactive for the production of aromatics from furans, this conclusion was based entirely on a predicted effect on the heterogeneous DA step of the reaction [113]. However, in a previous report on the formation of *p*-xylene from DMF and ethylene over the zeolite H-Y in heptane at 250 °C and 200 psi of ethylene, the DA step of the tandem scheme was, in fact, shown to proceed uncatalyzed in the homogeneous phase (heptane) [126]. Therefore, it remains to be determined whether H-[B]-BEA would be an ineffective catalyst for *p*-xylene production and what its effects on aromatic selectivity would be. Given the potential of increasing the selectivity to aromatics by replacing the Brønsted acid sites of zeolites with Lewis acid sites [29, 32, 127], in this work, we have investigated the effect of the Brønsted acid strength of solid acid zeolites on the production of aromatics. Toward this end, we used electronic structure calculations to parametrize a microkinetic model to make direct comparisons with experimental measurements. We investigated the Diels-Alder cycloaddition, dehydration, and hydrolysis reactions of furan, MF, and DMF in H-[B]-, H-[Fe]-, H-[Ga]-, and H-[Al]-BEA zeolites and made comparisons to experiments run for furan and DMF with H-[B]- and H-[Al]-BEA. We demonstrate, for the first time, that, despite its lower activity for alcohols, such as methanol and 2-propanol, H-[B]-BEA has an activity similar to that of H-[Al]-BEA for the production of aromatics from furans and ethylene.

4.2 Methods

4.2.1 Computational modeling

4.2.1.1 Electronic structure calculations

The BEA model was constructed by substituting B, Al, Fe, or Ga in the T5 position of the BEA unit cell and incorporating a proton on an adjacent oxygen atom in the lowest-energy configuration [76]. A cluster was cut from the larger crystal structure by selecting atoms in the first five tetrahedral coordination spheres surrounding the substituent atom and saturating all terminal silicon atoms with hydrogen atoms at a bond distance of 1.47 Å along the bond vector of the deleted crystal oxygen atoms. The model contained 111 tetrahedral atoms (111T) with stoichiometry [Al/B/Ga/Fe]Si₁₁₇O₁₈₀H₁₁₂ (Figure C.1 of Appendix C). Three ONIOM layers were then built from coordination spheres of tetrahedral atoms surrounding the T5 site; the small layer (16T) was allowed

to relax and was treated at the M06-2X/6-311G(2df,p) level of theory, the intermediate layer (18T) was frozen and treated at the M06-2X/6- 31G(d,p)//M06-2X/3-21G level of theory, and the real layer (77T) was frozen and treated with the universal force field (UFF) molecular mechanics theory [77, 78, 81, 116, 126]. Freezing of the intermediate and real layers sped calculations, maintained the zeolite structure, and eliminated spurious negative frequencies observed in some systems when these layers were allowed to relax. Specific details on the development of the mechanically embedded three-layer (QM/QM/MM) ONIOM model zeolite can be found in our recent publication [126]. Systems containing B, Al, or Ga were calculated with a spin multiplicities of 2, 4, and 6, we found the latter to be the lowest in energy. The full three-layer ONIOM model and the local structures of the B-, Al-, Fe-, and Ga-substituted H-BEA zeolites are shown in Figures C.1 and C.2 of Appendix C.

Solution-phase calculations of isolated reactants and products were performed with the SMD model of tetrahydrofuran (THF) at the M062X/6-311G(2df,p) level of theory [117]. THF was used as the solvent instead of heptane [21, 127] because furan is not soluble in heptane. Adsorbates within the pore were treated as part of the small layer. The binding energies were corrected for the basis set superposition error (BSSE), which was calculated for the high layer alone (including the adsorbates) by isolating it from the final full ONIOM model structure [138, 139]. The thermal corrections to the electronic energies were computed using the q-RRHO (quasi-rigid rotor-harmonic oscillator) approximation of Grimme and of Head-Gordon and coworkers [71, 89]. Thermodynamic quantities were calculated for adsorbates considered to have twodimensional translational degrees of freedom within the pore of a stationary zeolite with a characteristic area of $800 \times 800 \text{ pm}^2$ [97]. DFT calculations were carried out in the Gaussian 09 (Rev D.1) suite of programs [80].

Two reaction pathways have been studied: first, the Diels- Alder cycloaddition and subsequent dehydration to benzene, toluene, and p-xylene from furan, MF, and DMF, respectively, reacting with ethylene and, second, the hydrolyses of furan, MF, and DMF. Reaction profiles in zeolites with B, Ga, and Al framework atoms were run for all furan, MF, and DMF reactions. Additionally, the dehydration and hydrolysis reactions with DMF were run with framework Fe. Ground and transition states were characterized by frequency analysis, and all transition states were further validated by intrinsic reaction coordinate (IRC) calculations [140]. Bader analysis of the systems was performed using the AIM2000 software [141].

4.2.1.2 Microkinetic modeling

A microkinetic model (MKM) was constructed and parametrized based on the free energies calculated from the electronic structure calculations for furan and DMF in H-[Al]-BEA and H-[B]-BEA. The reaction network included the following pathways: homogeneous and heterogeneous Diels-Alder cycloaddition; homogeneous and heterogeneous dehydration of the cycloadduct; heterogeneous hydrolysis; and adsorption/desorption of all reactants, products, and stable intermediates onto and from the active site.

4.2.2 Experimental system

4.2.2.1 Materials

H-[Al]-BEA catalyst was obtained by heating the ammonium form of zeolite BEA (Zeolyst, CP814E) at 1 K min⁻¹ to 823 K and holding for 12 h in a furnace oven.

[B]-BEA was synthesized by forming a gel with the following composition: 5 B(OH)₃/73 SiO₂/20 tetraethylammonium hydroxide (TEAOH)/1000 H₂O. Boric acid (Sigma-Aldrich) and tetraethylammonium hydroxide (35% w/w aqueous solution, Alfa Aesar) were added to deionized water with constant stirring. Once the boric acid had completely dissolved, silicon dioxide (Cabosil M5) was slowly added to the solution. After all of the silicon dioxide was incorporated, the gel was stirred for an additional 15 min. [B]-BEA seed crystals (2% w/ w SiO₂ in gel) were added to the gel and stirred for 5 min. The resulting gel was then placed into the Teflon liner of a Parr 4744 autoclave and heated statically at 423 K for 14 days. The zeolite particles were filtered and washed with deionized water until the filtrate reached neutral pH. After being dried overnight at 353 K, the zeolite was calcined in air using the following temperature program: ramp from room temperature to 393 K in 1 h, hold at 393 K for 2 h, ramp from 393 to 823 K in 3 h, and final hold at 823 K for 5 h. Following calcination, an ion exchange was carried out overnight at room temperature in 0.05 M ammonium acetate (Fisher). The amount of ammonium acetate used was 5 times the amount of boric acid added to the gel on a molar basis [approximately 6.2 g of $NH_4CH_3CO_2$ per 1 g of $B(OH)_3$ in the gel]. The zeolite was then filtered and rinsed three times in deionized water and dried overnight at 353 K.

Zeolite chemical compositions were determined by inductively coupled plasma atomic emission spectrometry (ICPAES) at Galbraith Laboratories, Inc. (Knoxville, TN). Surface areas and microporous volumes (calculated using the t-plot method) were determined from N_2 adsorption isotherms measured using a Micromeritics 3Flex system. The samples were degassed overnight at 523 K and backfilled with nitrogen prior to analysis. Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 X-ray diffractometer with a Cu K α source ($\lambda = 1.542$ Å). Diffraction patterns were obtained using a step size of 0.02° (2 θ) with a 1-s counting time at each step and were measured between 5° and 50° (2 θ). SEM images were recorded with a JSM-7400F scanning electron microscope with an accelerating voltage of 3.00 kV and a current of 10 μ A.

4.2.2.2 Experimental details

In Diels-Alder cycloaddition and dehydration experiments, 1.92 g of dimethylfuran (Aldrich, 99%) or 1.36 g of furan (Acros, >99%) in 16.0 or 16.5 g of tetrahydrofuran (Fisher) was combined with 0.1 g of H-[Al]- BEA catalyst (Si/Al₂ = 25, Zeolyst) or 0.14 g of [B]-BEA (Si/ B_2 = 36) in a 50 mL 4790 Parr reactor with a magnetic stir bar. The reactor was sealed and purged with nitrogen gas and then filled with ethylene gas to 400 psi. The reactor was heated to 503 K with a ceramic band heater using a 30-min ramp time (not included as part of the reaction time). After the desired reaction time, the reaction was quenched by placing the reactor in an ice bath. Results reported for different reaction times (1, 5, and 24 h) are from separate experiments and not from multiple time points during the same experiment. The reaction product was filtered from the catalyst with a 0.2-µm filter. Product samples were analyzed with a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector. An HP-Innowax column (Agilent) was used with the following temperature program: hold at 313 K for 4.5 min, 10 K min⁻¹ ramp to 523 K, and final hold for 3 min. Reaction side products were identified with a GC/MS instrument (Shimadzu QP2010 Plus) equipped with an HP-Innowax column following the same temperature program. Calibrations for reactants and products (dimethylfuran, furan, para-xylene, and benzene) were determined from calibration solutions of each compound. GC response factors for 2,5hexanedione and 3-methyl-2-cyclopentenone were estimated to be the same as that of 2,5- dimethylfuran. The GC response factors of meta-xylene and the cycloadduct were estimated to be the same as that of *para*-xylene. The GC response factor for the alkylated xylene product was estimated by extrapolating the response factors of benzene, toluene, and xylene with increasing carbon number. The cycloadduct of furan and ethylene was estimated to have the same GC response factor as benzene.

A 300 μ L sample was taken for analysis prior to the reaction to determine the initial reactant concentration. The conversion of the furan starting material (dimethylfuran or furan) was determined as

$$conversion (\%) = \frac{c_{initial} - c_{final}}{c_{initial}} \times 100$$
(4.1)

where concentrations, C, are in moles per liter. Product yield was determined in the same units as

yield (%) =
$$\frac{C_{product}}{C_{furan,initial}} \times 100$$
 (4.2)

Finally, product selectivity was determined in the same units as

selectivity (%) =
$$\frac{C_{product}}{C_{furan, initial} - C_{furan, final}} \times 100$$
 (4.3)

4.3 **Results and Discussion**

4.3.1 Acidic properties of the catalysts

Characterization of acid strengths of solid acid zeolites, both experimentally and computationally, has been studied extensively (see [113, 130-134, 142], for example). In general, these studies have shown that changing the framework metal atom in a zeolite results in a change in its Brønsted acid strength, with the trend in strengths of
$[B] \ll [Ga] < [Fe] < [Al] [113, 130-134, 142].$ To compare our ONIOM model to this expected trend, we performed a detailed analysis of the intrinsic and extrinsic properties of our system (see Figures C.2 and C.3 and Table C.1 of Appendix C).

A measure of the acid strengths of Brønsted-acidic zeolites is the deprotonation energy (DPE), defined as

$$DPE = G_{Z^{-}} + G_{H^{+}} - G_{HZ} \tag{4.4}$$

where G_{Z^-} , G_{H^+} , and G_{HZ} are the energies of the zeolite anion after deprotonation, the gaseous proton, and the neutral H-form of the zeolite, respectively.

As can be seen in Table 1, H-[B]-BEA has a larger DPE (285 kcal/mol) than H-[Al]-, H-[Ga]-, and H-[Fe]-BEA (271-274 kcal/mol). Bader analysis revealed that this difference in DPE correlates with differences in the electron density of the O-H bond (Figure 4.3). At the bond critical point (BCP) of the O-H group, the negative of the Laplacian of the electron density is positive, which is indicative of covalent bonding [143]. A decrease in the electron density at the BCP leads to a weaker covalent bond, which scales linearly with the calculated DPEs. This correlation is consistent with other studies with an expected acid strength trend of [B] \ll [Ga] \approx [Fe] < [Al] [135].

4.3.2 Diels-Alder and dehydration reactions

For all three furans, the uncatalyzed Diels-Alder enthalpy barriers were found to be about 23.7 kcal/mol with respect to the marginally stable interacting complex of the addends. A representative enthalpy profile for the dehydrative aromatization of DMF and ethylene to *p*-xylene can be seen Figure 4.4; the enthalpy profiles for all of the systems tested here are provided in Table 4.2 (free energy profiles can be found in Figure C.4 and Table C.2 of Appendix C). Even though Brønsted acids catalyze certain

Framework Substituent	В	Fe	Ga	Al
Deprotonation Energy (kcal/mol)	285.4	274.7	274.5	271.8
<i>O-H Bond Critical</i> <i>Point Density</i> (a.u.)	0.351	0.338	0.337	0.337
O-H Bond Critical Point Laplacian (a.u.)	0.617	0.600	0.599	0.598

Table 4.1. Deprotonation energies and properties of the O-H bond critical point (BCP)for BEA with different framework metal substituent atoms.



Figure 4.3. Deprotonation energy (DPE) versus electron density and negative of the Laplacian of the electron density evaluated at the O-H (3,-1) bond critical point (BCP) in H-[B]-, H-[Fe]-, H-[Ga]-, and H-[Al]-BEA zeolite systems.

Diels-Alder reactions [28, 144] by a mechanism readily explained in terms of frontier molecular orbital theory [114, 145, 146], they *cannot* catalyze the DA reactions of furans and ethylene [19, 26, 27, 126]. Addition of furans to these zeolites results in the protonation of the furan ring even at low temperatures, as evidenced by the color change seen for DMF in Figure C.5 of Appendix C. In general, the proton has a much higher



Figure 4.4. Reaction profiles for the Diels-Alder cycloaddition and dehydration of DMF and ethylene to p-xylene and water over BEA zeolites with B, Ga, Fe, and Al framework metal-atom substituents.

affinity for the rings of furan, MF, and DMF (α -positions) than for ethylene [27],which changes the requisite molecular orbital symmetry needed for the [4+2] cycloaddition of the furan with ethylene. As a result, the reaction proceeds with *unprotonated* addends for all four zeolites tested in this study, with computed enthalpy barriers in the 23.6-26.3 kcal/mol range (Table 4.2), that is, close to or somewhat higher than the uncatalyzed barriers. In other words, the catalysts have no effect on the electronic distributions of the addends or on the charge transfer in the Diels-Alder transition state.

When entropy is taken into account, modest confinement effects on the cycloaddition can be observed. At high coverage of DMF on the surface (where the rate depends on the activity of the catalyst and the apparent activation energy is nearly identical to the intrinsic one), the free energies of activation are somewhat lower than the *ca*. 41 kcal/mol value of the uncatalyzed reaction, specifically, *ca*. 36 kcal/mol for

		DMF + F	Diels-Alder	Dehydration			
		Adsorption	Cycloaddition	C-O Cleavage	1 st Proton Transfer	2 nd Proton Transfer	
	Catalyst	$\Delta \mathbf{H}_{ads}$ (kcal/mol)	$\Delta \mathbf{H}^{\ddagger}_{\mathbf{forw}} // \Delta \mathbf{H}^{\ddagger}_{\mathbf{rev}}$ (kcal/mol)	$\Delta \mathbf{H}^{\ddagger}_{\mathbf{forw}} // \Delta \mathbf{H}^{\ddagger}_{\mathbf{rev}}$ (kcal/mol)			
	Uncatalyzed	-0.3	23.6 // 32.6	59.7 // 57.8	49.5 // 55.9	45.5 // 72.4	
un.	H-[B]-BEA	-16.7	24.0 // 38.8	30.8 // 9.8	9.5 // 35.7	8.9 // 39.0	
Fun	H-[Ga]-BEA	-18.3	23.6 // 44.7	26.8 // 9.9	7.5 // 33.3	10.4 // 38.1	
	H-[Al]-BEA	-18.7	23.7 // 44.8	25.7 // 10.7	8.6 // 33.6	13.8 // 40.1	
yl	Uncatalyzed	-0.6	23.8 // 32.7	56.2 // 53.0	46.9 // 52.6	47.2 // 73.6	
F 1eth	H-[B]-BEA	-18.8	24.9 // 38.2	31.6 // 8.2	5.3 // 33.7	10.4 // 28.7	
M. M-h	H-[Ga]-BEA	-22.0	25.3 // 43.1	27.3 // 9.3	5.5 // 29.1	11.2 // 23.2	
Ν	H-[Al]-BEA	-22.0	25.7 // 42.3	24.6 // 11.1	7.7 // 30.3	11.9 // 22.7	
	Uncatalyzed	-0.6	23.8 // 32.7	60.7 // 58.6	48.6 // 56.0	47.4 // 71.1	
F hyl	H-[B]-BEA	-20.5	23.8 // 34.7	25.2 // 7.7	12.2 // 34.3	8.7 // 37.6	
Met	H-[Ga]-BEA	-22.5	23.1 // 39.6	18.4 // 7.9	9.1 // 27.9	11.1 // 22.4	
	H-[Al]-BEA	-23.0	24.8 // 41.5	17.5 // 8.7	9.9 // 25.6	8.4 // 32.4	
	Uncatalyzed	-0.8	23.9 // 32.9	57.1 // 53.7	46.1 // 52.7	48.9 // 71.7	
MF	H-[B]-BEA	-21.1	25.8 // 37.0	23.6 // 6.7	8.3 // 33.9	12.9 // 27.3	
	H-[Ga]-BEA			18.9 // 8.5	7.6 // 27.7	12.5 // 19.2	
Γ	H-[Fe]-BEA	-23.5	26.3 // 43.8	17.9 // 8.6	8.0 // 24.9	9.8 // 18.9	
	H-[Al]-BEA	-23.4	26.2 // 41.1	14.2 // 9.6	8.6 // 24.0	9.1 // 17.8	

Table 4.2. Reaction profile energies for the Diels-Alder cycloadditions and dehydrations of furan, MF, and DMF on B-, Ga-, Fe-, and Al-substituted BEA zeolites.

furan, *ca.* 37 kcal/mol for MF, and *ca.* 39 kcal/mol for DMF (detailed values for all catalysts are reported in Table C.2). This modest drop in free energy of activation is not, however, sufficient for the heterogeneous Diels-Alder reaction to make a substantial contribution to the overall rate of the tandem scheme. Even at high acid-site concentrations (*i.e.*, low coverages), the rate is determined by the homogeneous Diels-Alder reaction, on account of the very low affinity of the zeolitic acid for furans [126, 127]. Consequently, in general, we do not expect the Brønsted acid functionality of the solid acid zeolites to affect the rate of the Diels-Alder step.

In contrast, Brønsted-acidic zeolites have a significant effect on the dehydration of the cycloadduct, an oxanorbornene derivative [19, 26, 27, 126]. The first and usually slowest step of this dehydration reaction (opening of the C-O bridge) requires an activation enthalpy in the range of 14-30 kcal/mol, depending on the furan and the catalyst, compared with the 60 kcal/mol of the uncatalyzed reaction (see Figure 4.4 for DMF and Table 4.2 for all of the systems). For a given furan, the dehydration barriers are significantly larger in H-[B]-BEA (25.4-30.8 kcal/mol) than in H-[Al]-, H-[Ga]-, and H-[Fe]-BEA (14-27 kcal/mol), but not so high as to completely stop the reaction. In addition, it is harder to cleave the C-O bridge of the cycloadduct formed from furan and easier to cleave the C-O bridge when the C atom has an electron-donating group, as in the cases of MF and DMF. For example, 7-9 kcal/mol more energy is required to break the C-O bridge on the unsubstituted side of the bridge of the cycloadduct formed from MF (Table 4.2).

It is instructive to consider the proton-catalyzed C-O bond cleavage in relation to the acidity of the active site and to the framework metal atom. For all but the strongest Brønsted acidic zeolite, H-[Al]-BEA, the cycloadduct proton affinity is not high enough to accept the proton of the active site upon adsorption, shown for the cycloadducts from furan and DMF in Figures 4.5(a) and (b), respectively. For B, Ga, and Fe, optimization calculations started with the proton on the bridge oxygen of the cycloadduct relaxed to the state with the proton back to the active site [confirmed by natural bond orbital (NBO) analysis]. Conversely, for H-[Al]-BEA, optimization calculations started with the proton on the active site relaxed to the state with the proton on the cylcoadduct bridge oxygen (also confirmed by NBO analysis). As the bridge C-O bond in the cycloadduct was cleaved, we observed a concurrent proton transfer to the cycloadduct



Figure 4.5. Active site coordinated cycloadducts of furan (a) and DMF (b) in H-[B]-BEA and H-[Al]-BEA zeolites and C-O cleavage transition states of furan (c) and DMF (d) in H-[B]-BEA and H-[Al]-BEA zeolites. Atoms in the zeolite framework beyond the first tetrahedral coordination sphere have been hidden for clarity. All bond distances shown are in angstroms.

for all of the zeolites studied (see Figures 4.5(c) and 4.5(d) for furan and DMF, respectively). Even for the H-[Al]-BEA system, for which coordination of the cycloadduct to the active site involves transfer of the active-site proton, the acceptor O-H bond length was found to decrease by 0.09 Å as the transition state of the C-O bond cleavage was reached.

The situation is reminiscent of enforced general acid catalysis in homogeneous and enzymatic systems, which involves a kinetically significant proton transfer that traps the intermediate [147, 148]. In homogeneous general acid catalysis, the activation energy is related to the pK_a of the acid through the *Brønsted catalysis law*, a linear relationship with a proportionality constant, α , whose value (between 0 and 1) represents the sensitivity of the reaction to the strength of the acid and reflects the extent of proton transfer in the transition state of the rate-determining step.

$$\log k = \alpha \log(K_a) + C \tag{4.5}$$

In early transition states (strongly exothermic reactions), α takes on small values (less than 0.5) and the proton does not transfer to the substrate. In late transition states (strongly endothermic reactions), α is close to unity, and the proton transfer is nearly complete in the transition state; intermediate values indicate that the proton is midway between the donor and the acceptor in the transition state.

We found a similar linear correlation between the activation free energy for C-O cleavage and the DPE of the active site (see Figure 4.6(a) for the various furans). Clearly, the barrier increases with the DPE of the acid site, that is, it increases with decreasing acid strength. The proportionality constant was found to be 0.8 for cleavage of the bridge on the substituted side, which is quite consistent with the geometry of the transition state, where we see nearly complete proton transfer (Figure 4.5(d)). For cleavage on the unsubstituted side of the bridge, the proportionality constant was found to be *ca*. 0.5, which would suggest partial proton transfer in the transition state; Figure 4.5(c), however, shows a nearly complete proton transfer in the transition state. Nevertheless, these correlations suggest that the dehydration rate should be moderately to strongly dependent on the acid strength and, thereby, subject to modulation. In contrast to the case for C-O cleavage, the subsequent reaction barriers of the dehydration mechanism, such as the first intramolecular proton transfer shown in Figure 4.6(b), are no longer dependent on the acid-site strength, with proportionality constants of ca. 0.1.



Figure 4.6. (a) C-O cleavage barrier and (b) frist intramolecular proton transfer barrier as functions of zeolite deprotonation energy (DPE) for oxanorbornene intermediates formed from furan, MF, and DMF. Solid symbols represent the dehydrations of furan and MF on the unsubstituted side of the oxanorbornene bridge, whereas open symbols represent the dehydrations of DMF and MF on the substituted side of the bridge.

Examination of the electron density of the cycloadduct in the uncatalyzed and Brønsted-acidic zeolites provides some insight into the catalytic effects. As can be seen qualitatively in Figure 6a, adsorption onto the active site was found to cause a depletion of electron density in the adsorbate. Progressive depletion of the electron density around the C-O bond with increasing acid strength was also observed. This is quantified in Figure 4.7(b), where we use Bader analysis and plot the electron density and the Laplacian of the electron density at the C-O BCP against the enthalpy of activation. The negative of the Laplacian at the BCP is positive, indicative of a covalent-type bond [143], with a decrease in electron density correlating to a weaker bond and smaller C-O cleavage barrier.



Figure 4.7. (a) Electrostatic potential mapped onto the electron density isosurface with value of 0.05 a.u. for the active site coordinated oxanorbornene intermediates and (b) C-O cleavage barrier as a function of the density and the negative of the Laplacian of the density evaluated at the C-O bond critical point.

4.3.3 Hydrolysis reaction step

The mechanism of furan hydrolysis in aqueous acidic media was studied by Nikbin *et al* [118]. In agreement with experiment, they showed that the reaction follows general acid catalysis, with the proton transfer from the acid to the β -C of the furan being the rate-determining step [149]. The subsequent nucleophilic attack by water at the α -C of the ring is practically nonactivated. A proton transfer from the added water to the γ -C of the ring completes the reaction. Formally, the reaction follows the same mechanism when it takes place in Brønsted-acidic zeolites. However, the kinetics, that is, the rate-determining step, is in large measure determined by the number of water molecules present in the vicinity of the active site. Using Monte Carlo methods, Xiong

et al. recently studied the coadsorption onto zeolite H-FAU of DMF, ethylene, *p*-xylene, and water from heptane solvent and concluded that some of the water produced from the dehydration of the oxanorbornene intermediate can remain in the pore, specifically, one to two molecules per unit cell [150]. In the following discussion, we detail the mechanism in the case of DMF and identify differences between pathways with one and two water molecules; H-BEA can readily accommodate two water molecules in the vicinity of the active site.

In Figures 4.8(a) and 4.8(b) we show the DMF hydrolysis enthalpy profiles with one and two water molecules, respectively, in H-[B]-BEA and H-[Al]-BEA. In both materials, proton transfer from the active site is more facile than the subsequent nucleophilic water addition when only one water molecule (the one being added) is included, making the water addition the rate-limiting step. In H-[B]-BEA, the proton transfer has an activation barrier of ca. 16 kcal/mol, whereas the water addition requires ca. 22 kcal/mol; in H-[Al]-BEA, the respective barriers are ca. 6 and 22 kcal/mol. Note that proton transfer in H-[B]-BEA is slower than that in H-[Al]-BEA, on account of the former being a weaker acid, whereas the water addition activation energy is practically independent of catalyst for all systems tested here (see also Table 4.3 for the protonation and water addition values for furan and MF in the different zeolites and Figures C.6 and C.7 and Table C.3 of Appendix C for the corresponding free energy profiles).

Inclusion of two water molecules has a dramatic effect on the energetics of the two steps. The proton transfer now becomes the rate-limiting step, with barriers of ca. 8 kcal/mol in H-[A1]-BEA and 19 kcal/mol in H-[B]-BEA, whereas the water addition is practically nonactivated, with respective barriers of 1.0 and 1.4 kcal/mol. This change in reaction barrier for the nucleophilic attack by water is attributable to strain imparted



Figure 4.8. Reaction profiles for the hydrolyses of DMF on B- and Al-substituted BEA zeolites with (a) one or (b) two explicit water molecules in the pore.

to the protonated furan molecule during this concerted reaction step. With one water molecule (Figure 4.9), the γ -C of the furan accepts a proton from the added water. The inclusion of a second water molecule mediates the proton transfer and this greatly reduces the strain. These results are in agreement with those of Li *et al.*, who showed the protonation of furan to be the rate-limiting step for hydrolysis in H-[Al]-BEA [113].

In their mechanism, a single water molecule displaces the protonated furan from the active site, so that the hydrogen from the water is transferred back to the zeolite rather than to the γ -C of the furan.

The energetics above reveal that the hydrolysis of furans in Brønsted-acidic zeolites follows the kinetics of general acid catalysis, in manner similar to that of the homogeneous reaction in aqueous acidic media [118]. In their physisorbed states, furan and DMF do not abstract the proton from the zeolite (Figures 4.10(a) and 4.10(b)). β -C protonation results in the transfer of a proton from the zeolite to the furan or DMF, with a sharing of the proton in the transition state (Figures 4.10(c) and 4.10(d)). A correlation similar to that identified earlier for cycloadduct dehydration is shown in Figure 4.11(a) for proton transfer from the active site to the furan. In the case of furan, the weakest proton acceptor of the three furans tested, the proportionality constant between the free energy of activation for proton transfer and the DPE of the acid is about 0.7, suggesting rather partial proton transfer in the transition state and rather strong sensitivity to the strength of the acid. In the cases of DMF and MF, the proportionality constant increases to 0.8. Once the proton has been transferred, the nucleophilic attack by water becomes independent of the catalyst, with proportionality constants close to zero (Figure 4.11(b)).

4.3.4 Experimental results

For comparison to computational results, furan and DMF were tested experimentally for DA cycloaddition and dehydration over H-[Al]-BEA and H- [B]-BEA. H-[Al]-BEA (Si/Al = 12.5) was obtained from a commercial source, and H-[B]-BEA was synthesized in-house. The Si/B ratio of the H-[B]-BEA was *ca.* 18 as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES)

		Hydrolysis – 1 H ₂ O		Hydrolysis – 2 H ₂ O		
	Catalyst	∆H _{ads} (kcal/mol)	β -C Protonation $\Delta H^{\ddagger}_{forw} // \Delta H^{\ddagger}_{rev}$ (kcal/mol)	$\Delta \mathbf{H}_{ads}$ (kcal/mol)	<mark>β-C Protonation</mark> ΔH [‡] _{forw} // ΔH [‡] _{rev} (kcal/mol)	
	Uncatalyzed	-12.8	27.3 // 0.8	-14.8	21.2 // -1.4	
an	H-[B]-BEA	-15.4	19.6 // 1.5	-19.6	14.6 // -0.8	
Fur	H-[Ga]-BEA	-15.7	17.8 // 2.2	-20.0	12.9 // 5.2	
	H-[Al]-BEA	-10.4	20.2 // -1.1	-20.8	25.7 // 4.5	
yl	Uncatalyzed	-13.3	12.4 // -1.4	-21.2	12.4 // 3.8	
F 1eth	H-[B]-BEA	-13.5	11.2 // 0.6	-19.8	13.8 // 7.3	
M Non-M	H-[Ga]-BEA	-10.2	14.9 // 0.9	-22.2	22.1 // 3.6	
	H-[Al]-BEA	-18.8	15.0 // 5.6	-23.1	8.6 // 5.9	
	Uncatalyzed	-18.8	13.6 // 6.6	-18.4	7.6 // 6.3	
MF Methyl	H-[B]-BEA	-14.5	16.1 // 1.8	-21.0	19.0 // 8.4	
	H-[Ga]-BEA	-16.9	7.4 // 2.5	-20.6	8.7 // 9.0	
	H-[Al]-BEA	-15.3	6.6 // 2.9	-21.6	9.0 // 9.2	
	Uncatalyzed	-15.4	5.6 // 4.0	-21.1	7.9 // 10.3	
MF	H-[B]-BEA	-12.8	27.3 // 0.8	-14.8	21.2 // -1.4	
	H-[Ga]-BEA	-15.4	19.6 // 1.5	-19.6	14.6 // -0.8	
Γ	H-[Fe]-BEA	-15.7	17.8 // 2.2	-20.0	12.9 // 5.2	
	H-[Al]-BEA	-10.4	20.2 // -1.1	-20.8	25.7 // 4.5	

Table 4.3. Reaction profile energies for the hydrolysis of furan, MF, and DMF on B-,Ga-, Fe-, and Al-substituted BEA zeolites.



Figure 4.9. Transition-state structure for the nucleophilic attack of DMF by water in H-[Al]-BEA with (a) one and (b) two explicit water molecules in the pore. The surrounding zeolite pore has been removed from the image for clarity.



Figure 4.10. Active-site-coordinated structures of (a) furan and (b) DMF in H-[B]-BEA and H-[A1]-BEA zeolites and transition states of protonation of the β -C of (c) furan and (d) DMF in H-[B]-BEA and H-[A1]-BEA zeolites. Atoms in the zeolite framework beyond the first tetrahedral coordination sphere have been hidden for clarity. All bond distances shown are in angstroms.

analysis. XRD patterns for both materials can be found in Figure C.8 of Appendix C, and both are consistent with the BEA framework. The micropore volume of each material was measured by nitrogen physisorption. The micropore volume of H-[Al]-BEA was 0.18 cm³/g, and that of H-[B]-BEA was 0.23 cm³/g. The micropore volume of H-[B]-BEA is consistent with that reported in previous studies on H-[B]-BEA [151]. SEM images are also included in Figure C.9 of Appendix C [151]. Whereas previous studies have used heptane as the solvent, in this work tetrahydrofuran (THF) was used because furan is immiscible with heptane and it was previously reported that higher



Figure 4.11. (a) β -C protonation barrier and (b) nucleophilic attack barrier as functions of the zeolite deprotonation energy (DPE) for furan, MF, and DMF. Free energy reaction barriers, rather than enthalpy barriers, are used to make a direct comparison with the Brønsted catalysis law, which is dependent on kinetics rather than energetics alone. Solid symbols represent the dehydrations of furan and MF on the unsubstituted side of the oxanorbornene bridge, whereas open symbols represent the dehydrations of DMF and MF on the substituted side of the bridge.

yields of p-xylene can be obtained with THF than with heptane [152]. Because of the slight difference in heteroatom incorporation in the B and Al materials, a higher weight of H-[B]-BEA than of H-[Al]-BEA was used so that the amounts of active sites in the two reactions would be the same.

Experimental results for furan and DMF DA cycloaddition and dehydration on H-[B]-BEA and H-[AI]-BEA can be found in Table 4.4. The main byproduct detected with furan had a molecular weight consistent with the Diels-Alder cycloadduct (MW = 96). It is unclear whether this is the true oxanorbornene intermediate as it is possible

Furan Zeolite	Furan H-[B]-BEA	Furan H-[Al]-BEA	DMF H-[B]-BEA		DMF H-[Al]-BEA			
Time (hr)	5	5	1	5	24	1	5	24
Furan Conversion (%)	20.2	25.3	9.8	57.6	96.7	12.3	53.6	94.9
Aromatic ^a Yield/Select. (%)	3.6 / 18.0	4.7 / 18.6	6.0 / 61.1	40.9 / 71.0	68.5 / 70.8	4.2 / 33.8	33.8 / 63.1	66.4 / 70.0
Cycloadduct Yield/Select. (%)	4.2	4.5	0	0.7	2.3	0.1	2.1	4.5
m-Xylene Yield (%)			0	0.3	0.6	0	0.3	0.4
Alkylated Xylene Yield (%)			0.5	2.1	3.6	0.1	0.5	2.3
2,5-Hexanedione Yield (%)			0.4	3.6	0.7	2	3.7	1.1
3-Methyl-2- Cyclopentanone Yield (%)			0	0.3	0	0.9	2.8	3.4
Carbon Balance (%)	87.6	83.9	97	90.4	78.9	95	89.6	83.3
^a Benzene for furan	ı, and p-xylene f	for DMF						

Table 4.4. Experimental results for Diels-Alder cycloaddition and dehydration of furanand dimethylfuran, 250°C and 400 psi C2H4 in a batch reactor.

that this intermediate would not survive the high temperatures of the GC analysis and would instead undergo retro-Diels-Alder. Nonetheless, a similar intermediate was identified as this adduct in a previous work, and this byproduct was thus treated similarly here [112]. The cycloadduct intermediate from cycloaddition of DMF and ethylene (MW = 124) was not found to be as significant a byproduct as when furan was the reactant. Instead, the hydrolysis pathway was found to provide two byproducts that affect xylene selectivity.

The product of hydrolysis of DMF is 2,5-hexanedione. A related byproduct is 3methyl-2-cyclopentenone, the intramolecular aldol condensation product of 2,5hexanedione. Although this was found to be a small byproduct (<3.4% yield) on H-[A1]-BEA, it was detected only at the 5-h time point on H-[B]-BEA and in a very small amount (0.3% yield). This suggests that the weaker acidity of H-[B]-BEA makes it a less effective catalyst than H-[Al]-BEA at catalyzing the intramolecular aldol condensation. The hydrolysis of DMF to hexanedione is reversible; however, the total yield of hexanedione and cyclopentenone was always found to be higher on H-[Al]-BEA than on H-[B]-BEA. A higher yield of overalkylated product (MW = 134) was found at every time point on H-[B]-BEA compared to H-[Al]- BEA, but not enough to match the loss to side products from hydrolysis on H-[Al]-BEA, resulting in the slight but distinctly higher yield and selectivity to *p*-xylene found on H-[B]-BEA at all of the time points measured.

In previous works comparing H-[Al]-BEA to solid Lewis acid zeolites such as [Zr]-BEA for DMF cycloaddition and dehydration to p-xylene, two kinetic regimes were described depending on the acid-site concentration [31, 127]. The first regime is linearly dependent on the acid-site concentration and limited by the dehydration of the cycloadduct. The second regime is independent of the acid-site concentration and limited by the uncatalyzed Diels-Alder cycloaddition. The acid-site concentration for the experiments performed in this work fall in the second regime. Although very different dehydration activities were expected for [Zr]-BEA and H-[Al]-BEA, similar rates of *p*-xylene formation were found when operating in the second, cycloadditionlimited regime. This is consistent with the results reported here, where the dehydration would be expected to be slower on H-[B]-BEA but the reaction rate was found to be very similar to that on H-[Al]-BEA, because, in the second regime, the overall reaction rate is controlled by the homogeneous DA step. Compared to DMF, furan results in much lower conversion and selectivity, as expected and as reported previously with heptane as the solvent [21]. Only one data point was collected for this system because of its low selectivity, which is expected to degrade further at longer reaction times [21].

Because the hydrolysis product of furan, butanedial, was not detected in the product, it is not possible to compare this pathway to that occurring with DMF. Most likely, the butanedial was not detected because it is very reactive and oligomerizes, contributing to low selectivity. The yields of benzene were very similar for both H-[B]- and H-[Al]-BEA, which, as in the case of DMF, is surprising considering the very different predicted strengths of acidity of the two materials.

4.3.5 Microkinetic modeling

The values used to parametrize the microkinetic model from electronic structure calculations can be found in Table C.4 of Appendix C. Using this microkinetic model for H-[B]-BEA and H-[Al]-BEA, the two extremes of acid strength, we made a direct comparison to experiment. As shown in Figure 4.12(a), both H-[B]-BEA and H-[Al]-BEA were predicted to be effective catalysts for aromatic production. For furan, the experimental conversion with both catalysts was *ca*. 20% after 5 h. The MKM predicted a lower-than-expected conversion with H-[B]-BEA at less than 5% after 24 h, whereas H-[Al]-BEA reached a conversion of *ca*. 15% after 5 h and *ca*. 50% after 24 h. This difference in rate can be understood by examining the sensitivity analysis of the model, shown in Figure 4.13. For furan in H-[B]-BEA, the heterogeneous dehydration reaction is the rate-limiting step, whereas for H-[Al]-BEA, the uncatalyzed DA reaction is rate-limiting. The C-O cleavage barrier of *ca*. 27 kcal/mol for furan in H-[B]-BEA is 10 kcal/mol larger than those of any of the other systems studied, leading to the lower predicted activity for this system.

The experimental conversions of DMF for both catalysts were *ca.* 60% after 5 h and *ca.* 80% after 24 h. The MKM-predicted conversions for DMF for both catalysts were very similar, reaching *ca.* 20% after 5 h and *ca.* 60% after 24 h. For both systems,



Figure 4.12. Comparison of MKM results (solid or dashed lines) with experiments (points) for (a) furan/DMF conversion over time (b) benzene and butanedial yields as functions of furan conversion, and (c) *p*-xylene and hexanedione yields as functions of DMF conversion in H-[B]-BEA and H-[A1]-BEA. (Solid circles are connected with thin lines to guide the eye in the case of DMF.)

as was the case for furan with H-[Al]-BEA, the homogeneous DA barrier was ratelimiting (Figure 4.13). The lower-than-expected DMF conversion rate with a homogeneous DA reaction suggests an overpredicted barrier in the system. In a recent study, we showed that the homogeneous DA barrier is overestimated by ca. 4 kcal/mol at the M06-2X/6- 311G(2df,p) level of theory in implicit heptane solvent relative to the more accurate CBS-QB3 level of theory [127]. This difference in the homogeneous DA barrier was sufficient to predict a *p*-xylene production rate of the correct order of magnitude with respect to experiment [127].

The agreement seen for furan in H-[A1]-BEA appears to be a fortunate circumstance, as confirmed by a closer examination of the benzene and butanedial yields as functions of furan conversion (Figure 4.12(b)). At 20% furan conversion, a 5% yield (25% selectivity) to benzene was observed with no butanedial production. The MKM, on the other hand, predicted benzene as the only product from furan



Figure 4.13. Sensitivity analysis performed on microkinetic models of furan and DMF in H-[B]-BEA and H-[Al]-BEA under the experimental conditions.

conversion, but with a 20% yield at 20% conversion. This lower-than-expected yield of benzene indicates that the model is failing to capture important side reactions in this process. Considering how much more accurate the microkinetic model is at describing *p*-xylene formation from DMF than at describing benzene formation from furan, we conclude that oligomerization reactions must be playing a significant role in the case of furan. This is also evidenced by the catalyst deactivation and color change seen experimentally and would need to be taken into account to improve the modeling results. Further investigations into oligomerization side reactions are beyond the scope of this report.

DMF shows a much better agreement with experiments over a larger range of conversions, as seen in Figure 4.12(c). Up to 50% conversion, *p*-xylene yields are *ca*. 40% for both systems, in excellent agreement with experiments. At this level of conversion, 2,5-hexanedione yields are predicted to reach a maximum of 5-10% with

both zeolites, again in good agreement with experiments. At close to 100% DMF conversion, a deviation from experiments is observed, as the MKM overpredicts the *p*-xylene yield by *ca*. 20%. This suggests that the oligomerization side reactions involved in catalyst coking are less significant for DMF than for furan, but contribute to deactivation at high conversions.

Examining furan reactants with and without methyl substituents in a range of Brønsted-acidic zeolites has allowed us to make some general observations about these catalysts for furan aromatization. First, even the weakest Brønsted-acidic zeolite studied, H-[B]-BEA, is an effective and active catalyst for these reactions by significantly lowering the dehydration reaction barrier. Experimentally, the conversion rates and product yields are very similar between the two zeolites studied, suggesting that the same pathways are active and catalyzed by both Brønsted-acidic zeolites studied. As long as the system contains Brønsted acid sites, reactants such as furan will be susceptible to these undesired side reactions.

Second, the presence of methyl substituents on the furan plays a significant role in reducing undesired oligomerization reactions in these systems. For furan, the benzene yields were significantly lower than the p-xylene yields for DMF, and catalyst deactivation was much faster. Without significant levels of butanedial predicted by the model or seen experimentally, the hydrolysis reaction cannot represent the major deactivation pathway. Rather, oligomerization reactions between reactants, products, or intermediates must play a significant role in these systems.

4.4 Conclusions

Electronic structure calculations and microkinetic modeling have been used to investigate the Diels-Alder cycloaddition and subsequent dehydration to aromatics of furan, MF, and DMF with ethylene in Brønsted-acidic zeolites. We were motivated by a desire to improve the aromatic selectivities from furan and MF by using a weaker Brønsted-acidic catalyst that could be less susceptible to side reactions and catalyst deactivation.

Electronic structure calculations showed a change in acid strength for these Brønsted-acidic zeolites with changing metal substituents, suggesting that H-[B]-BEA is a weaker acid than any of the other materials examined. A lack of catalysis of the DA reaction was seen for all Brønsted-acidic zeolites considered. For the dehydration and hydrolysis reactions, however, the Brønsted acid played an important role in catalyzing these reactions, following the principles of general acid catalysis. For these reactions, the nature and strength of the acid sites correlated with their reaction barriers.

Experimental runs tested the weakest and strongest Brønsted-acidic zeolites, H-[B]-BEA and H-[A1]-BEA, respectively, and found that both were active catalysts for aromatic production. Notably, they showed similar conversion rates and product yields, suggesting that weakening of the Brønsted acid sites did not significantly change the reaction mechanisms in the system. Using furan as a starting reactant led to a considerably lower selectivity to benzene, as compared to the selectivity to *p*-xylene from DMF, suggesting that side reactions play an important role in the former system. The absence of butanedial from the products in the case of furan, both in the MKM model and experimentally, revealed that side reactions other than hydrolysis of the furan, such as oligomerization, are more significant in this system, leading to decreased selectivity and increased catalyst coking and deactivation.

4.5 Acknowledgements

This material has been adapted with permission from Patet, R.E., Koehle, M., Lobo, R. F., Caratzoulas, S., Vlachos, D. G. General acid-type catalysis in the dehydrative aromatization of furans to aromatics in H-[Al]-BEA, H-[Fe]-BEA, H-[Ga]-BEA, and H-[B]-BEA zeolites. *J. Phys. Chem. C* **2017**, *In Press.*, Copyright 2017 American Chemical Society. I would like to thank the co-authors of this work, Molly Koehle and Prof. Raul Lobo for their contribution of materials therein related to experimental synthesis, characterization, and reactions. I would like the co-authors of this work, Dr. Stavros Caratzoulas and Prof. Dionisios G. Vlachos, for their contributions and insights related to the computational calculations and overall message of the manuscript.

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Chapter 5

TANDEM DIELS-ALDER OF DIMETHYLFURAN AND ETHYLENE AND DEHYDRATION TO PARA-XYLENE CATALYZED BY ZEOTYPIC LEWIS ACIDS

5.1 Introduction

Across the chemical industry, there is a push to discover new sources for the fuels and chemicals currently derived from fossil resources, and biomass is an ideal feedstock for a number of renewable monomers [4, 102, 105, 111, 119, 123-125, 153, 154]. As inexpensive natural gas liquids (shale gas) are pushing naphtha feedstocks aside, the development of alternative routes for the production of aromatics from renewables is receiving considerable attention [104, 109, 155, 156]. Of the possible routes is the dehydrative aromatization of the Diels-Alder (DA) product between biobased furans with an appropriate dienophile; a tandem scheme where the oxanorbornene derivative obtained from the DA cycloaddition is catalytically dehydrated to an aromatic (Figure 5.1). The strategy is showcased by the recently reported formation of *p*-xylene from 2,5-dimethylfuran (DMF) and ethylene over the Brønsted-acidic catalysts H-Y and H-BEA, with yields as high as 90% [19, 21, 112, 126]. The same approach was applied by Green et al.[128] to convert methylfuran and ethylene to toluene over H-BEA, but the selectivity did not exceed 46%, primarily because methylfuran was lost to side reactions (e.g., alkylation, hydrolysis and oligomerization) (Figure 5.1) [128]. Independently, Pacheco and Davis achieved Diels-Alder aromatization of ethylene and oxidized variants of HMF over isomorphically substituted Sn-BEA to form terephthalic



Figure 5.1. Diels-Alder aromatization of 2,5-dimethylfuran (DMF) and ethylene to *p*-xylene; and hydrolysis of DMF to 2,5-hexanedione.

acid, paving the road for renewable polyethylene terephthalate (PET) [9, 29, 30]. Orazov and Davis [33] have shown that CIT-6 (Zn-BEA), an easily synthesized zincosilicate analogue of zeolite BEA, can catalyze the Diels-Alder aromatization of ethylene and methyl 5-(methoxymethyl)-furoate to form methyl 4-(methoxymethyl)-benzoate, and that of ethylene and the dimethyl ester of 2,5-furandicarboxylic acid to form dimethyl terephthalate [33]. The work of Pacheco and Davis prompted Chang *et al.* [31] to investigate the Diels-Alder aromatization of DMF and ethylene to *p*-xylene over the Lewis-acidic zeotypes Sn-, Zr- and Ti-BEA. Remarkably, they found that these catalysts are just as effective as H-BEA in influencing the rate of the tandem scheme, while reducing the hydrolysis of DMF [26]. Among the tested catalysts, Zr-BEA exhibited superior performance with 80% selectivity to *p*-xylene at 80% conversion of DMF. Sn-BEA, Ti-BEA, and H-BEA, however, deactivated noticeably faster, and only achieved about 60% DMF conversion, with lower selectivity to *p*-xylene. The lower yields notwithstanding, the zeotypic Lewis acids exhibited longer lifetimes than H-BEA, attributed to low selectivity to the DMF hydrolysis product, 2,5-hexandione (which can oligomerize) and to low coke formation.

However, because of the fleeting existence of the cycloadduct in all these studies, kinetics experiments have not been able to decouple the two steps and thus elucidate whether these Brønsted- and Lewis-acidic zeotypes have any effect on the rate of the Diels-Alder step itself. With furans being among the less reactive dienes, overcoming the challenge of accelerating the cycloaddition reaction will be a pivotal step in the success of producing aromatics by Diels-Ader aromatization of biomassderived furans and appropriate dienophiles.

Brønsted and Lewis acids are known to accelerate a variety of DA reactions [28]. The mechanism by which they influence the rate of the DA reaction can readily be explained in terms of the frontier molecular orbital (FMO) theory [114, 145, 146, 157-160]. In normal electron demand, protonation or complexation with the Lewis acid of the dienophile lowers the energy of its LUMO and closes the gap to the HOMO of the diene, increasing the interaction between the two FMOs and thus the rate of the reaction. In recent years, Diels-Alder reactivity has also been rationalized in terms of the polar character of the transition state and of the concepts of electronic hardness and electrophilicity [161-169].

Calculations by Nikbin *et al.* [19, 26, 27] and by Patet *et al.* [126] have asserted that neither Brønsted nor alkali-exchanged Lewis acid zeotypes can influence the rate of the DA between DMF and ethylene. Brønsted-acidic zeolites, such as H-BEA or H-Y, cannot do so for a couple of reasons. First, DMF binds more strongly to the active site than ethylene. Second, the proton has higher affinity for the α -position of the furan ring instead of the O-heteroatom and thus protonation breaks the requisite orbital symmetry. A similar situation has been observed in alkali-exchanged zeolites, where calculations have shown that the preferred coordination of DMF to the active site *does* lower the LUMO of the furan, but not enough to activate the inverse electron demand mode and to compensate for the deactivation of the normal electron demand mode due to the concomitant lowering of the HOMO of DMF [26, 27, 170]. So, over alkali-exchanged zeolites, the reaction follows bi-directional electron demand (namely, both HOMO(diene)-LUMO(dienophile) and HOMO(dienophile)-LUMO(diene) driven [146]) with no noticeable acceleration. Although inverse electron demand cycloadditions have been reported, strong Lewis acids are required [163, 171, 172]. Alkali cations such as Li⁺ and Na⁺, with a large positive surface charge density, should in principle be effective Lewis acid catalysts [26, 144, 170], but when they are embedded in zeolitic frameworks, charge screening by surrounding framework oxygen atoms diminishes their catalytic activity [27].

It is an open question, however, whether the framework-substituted zeolites tested by Chang *et al.* [31] can catalyze the Diels-Alder between DMF and ethylene. Given the importance of the Diels-Alder cycloaddition as a tool in synthetic organic chemistry and, in particular, its significance for the development of a technology for the sustainable conversion of furans to aromatics, in this article we use electronic structure calculations and microkinetic modelling to study the Diels-Alder aromatization of DMF and ethylene in Sn-BEA, Zr-BEA, and Ti-BEA and assess their ability to catalyze Diels-Alder cycloaddition and the subsequent dehydrative aromatization.

5.2 Methods

5.2.1 Electronic structure calculations

In all the calculations the zeolites are modelled as mechanically embedded threelayer (QM/QM/MM) ONIOM clusters [37, 54, 77]. To build the model, a metal-atom (Sn/Ti/Zr) is substituted for a Si-atom in the T9 position of the BEA unit cell [76] and then a cluster is hewn out of the crystal by selecting the atoms in the first five tetrahedral coordination spheres surrounding the metal-atom. All dangling bonds are saturated with H-atoms for a model containing 118 tetrahedral atoms (118T) and a stoichiometry of [Sn/Ti/Zr]Si117O180H112 (shown in Figure D.1 of Appendix D). The small layer (17T) is allowed to relax and is treated at the M06-2X/6-311G(2df,p) theory level, with the metal atoms modelled with the LANL2DZ effective core potential [81]. All reactants, intermediates, and products are treated as part of this small layer. The intermediate layer (17T) is treated at the M06-2X/6-31G(d,p)//M06-2X/3-21G theory level and is frozen geometrically to maintain the zeolite pore structure integrity. The real layer (84T) is treated with the universal force field (UFF) molecular mechanics theory [116], and is also frozen geometrically. Relaxing the intermediate- and low-level layers led to spurious imaginary frequencies in certain calculations.

Both unhydrolyzed ("closed"), metal-(OSi)4), and partially hydrolyzed ("open"), ((HO-metal-(OSi)3), active sites are considered, as shown in Figures 5.2a and 5.2b [173]. Only closed sites of Ti-BEA are considered, as Ti-BEA is not thought to form open sites [174].

Solution phase calculations were performed using the SMD model [117] of heptane. Ground and transition states were characterized by frequency analysis and all transition states were further validated by intrinsic reaction coordinate (IRC)



Figure 5.2. "Closed" active site, and b) "open" active site representations of Sn-BEA. Surrounding atoms have been hidden for clarity. (H – white; Si – gray; O – red, Sn – purple).

calculations [80]. The thermal corrections to the electronic energies were computed using the q-RRHO (quasi-rigid rotor harmonic oscillator) approximation of Grimme [89] and of Head-Gordon [71].

More details on the development and benchmarking of the methodology can be found in our recent publication [139]. We should note that we have also performed single-point energy calculations at the M06-2X/Def2TZVP theory level for the small (high-level ONIOM) layer without a significant effect on the calculated free energy profiles (Table D.1 of Appendix D).

Natural population analysis (NPA) was performed with the NBO 6.0 software suite [175]. Bader analysis [143] was performed using the AIM2000 program. The NBO and Bader analyses were performed on the isolated ONIOM small layer (capped with H atoms and frozen in the geometry of the fully optimized ONIOM model).

5.2.2 Microkinetic modelling

A microkinetic model (MKM) has been constructed and parameterized based on the free energy profiles obtained from the electronic structure calculations. The reaction network includes the following pathways: homogeneous and heterogeneous Diels-Alder cycloaddition of DMF and ethylene; homogeneous and heterogeneous dehydration of the Diels-Alder product; heterogeneous hydrolysis of DMF; and the adsorption and desorption of all reactants, products, and stable intermediates onto and from the active site. For the open sites, we have allowed for two distinct catalytic pathways: the Lewis acidic metal site pathway and the Brønsted acidic pathway that involves the Si-OH group in the immediate vicinity of the metal site. For the closed active sites, only coordination to the metal site is considered.

5.3 Results

5.3.1 Characterization of the active site

In Table 5.1, we show geometrical parameters of the active site and the NPA charges of its atoms. The metal-framework oxygen bonds are longer that the Si-O bonds they are replacing, in the 1.8-1.9 Å range commensurately with the relative atomic size from *ca*. 1.6 Å for Si to for the metal substituents. This difference in atomic size causes a change in the local zeolite framework structure, as evidenced by the T-O-Si bond angle (where T represents Sn, Ti, or Zr), with the smallest substituent, Ti, resulting in the broadest angle of *ca*. 138° and to the largest, Zr, having a sharper angle of *ca*. 132°. A difference can be seen in the atomic charges of the incorporated metal atoms. The Sn and Zr atoms are more positively charged (+2.8 and +2.5) than Ti (+1.9). The change in structure from the closed to the open sites does not significantly change either the

Table 5.1. NBO analysis of Sn-, Ti-, and Zr-BEA closed and open active sites. The Si atom is that which is hydrolyzed into the Si-OH unit of the open site. The O-atom represents the bridging O in the closed site, and the O-atom taken as part of the Si-OH unit of the open site. The H-atom was taken as part of the Si-OH unit of the open site.

	Sn-BEA "Closed"	Ti-BEA "Closed"	Zr-BEA "Closed"	Sn-BEA "Open"	Zr-BEA "Open"
$Charge - T (q_T)^a$	2.84	1.95	2.54	2.85	2.53
$Charge-Si(q_{Si})$	2.57	2.57	2.56	2.50	2.49
$Charge - O\left(q_O\right)$	-1.33	-1.11	-1.25	-1.13	-1.10
$Charge - H(q_H)$				0.53	0.53
Bond Distance – T-O $(D_{T-O})^a$ (\AA)	1.84	1.76	1.91	2.01	2.14
Bond Distance – Si-O (D_{Si-O}) $(Å)$	1.59	1.60	1.59	1.80	1.79
Bond Angle – T-O-Si $(A_{T-O-Si})^a$ (°)	133.8	137.8	131.8	101.7	99.7
Bond Distance – O - $H(D_{O-H})(\mathring{A})$				0.96	0.96
Deprotonation Energy (kcal/mol)				284.6	298.2
$Charge-T(q_T)^a$	2.84	1.95	2.54	2.85	2.53
^{<i>a</i>} $T = Sn$, Ti , or Zr					

bond distances or atomic charges of these systems, although a change in the local structure is evident from a decrease in the T-O-Si angle to ca. 100°.

The Si-OH group of the open active site is moderately Brønsted acidic. The NPA charge of the H-atom is ca. +0.5 for all the zeotypic Lewis acids considered; and is also the same as the partial change of the Brønsted-acidic hydrogen atom of Al-BEA. However, the computed deprotonation energies (DPE) (see. Eq. 5.1) show a dependence on the metal atom. In the case of Zr-BEA the DPE is ca. 300 kcal/mol whereas for Sn-BEA it is ca. 285 kcal/mol, meaning that the latter has somewhat stronger Brønsted-acidic character. For perspective, the DPE of Al-BEA is 271.1 kcal/mol.

$$DPE = E_{Z-H} - E_{Z^-} - E_{H^+}$$
(5.1)

5.3.2 Catalysis of the Diels-Alder and dehydration reactions

The mechanism for the formation of p-xylene and water from DMF and ethylene is shown in Figure 5.3, whereby the oxanorbornene intermediate formed by Diels-Alder cycloaddition subsequently undergoes dehydration in three steps to form p-xylene [19, 26, 27, 126]. Enthalpy profiles for the closed active sites are shown in Figure 5.4a and for the open active sites in Figure 5.4b.

For the uncatalyzed Diels-Alder reaction in heptane, the reaction barrier is 24 kcal/mol at the M06-2X/6-311G(2df,p) theory level. A more accurate calculation of the uncatalyzed reaction at the CBS-QB3 theory level yields an enthalpy barrier of 20 kcal/mol. For all the catalysts considered, the Diels-Alder transition state is stabilized by 20-25 kcal/mol relative to the gas phase, depending on the active site metal center and on whether the site is hydrolyzed or not. We also see similar stabilization of the interacting complex of the two addends, with preferential coordination of the furan to the active site. Relative to the gas phase, the interactive complex is stabilized by ca. 20 kcal/mol on the catalysts with closed active sites (Figure 5.4a) and by ca. 20-25 kcal/mol on those with open sites (Figure 5.4b). As a result, the intrinsic DA enthalpy barriers, viz. relative to the active-site-coordinated interacting complex, remain in the 23-25 kcal/mol range - the same as in the uncatalyzed reaction. Thus, with the furan coordinated to the active site, the Lewis acid centers seem unable to induce sufficient charge transfer to promote inverse electron demand cycloaddition. We will later see that confinement and entropic phenomena may be more consequential to the adsorption and stability of the reactants and transition state complexes, and thereby to the Diels-Alder of furans with alkenes not bearing electron withdrawing groups.



Figure 5.3. Reaction mechanism for the Diels-Alder cycloaddition of DMF and ethylene, and subsequent three-step dehydration to water and *p*-xylene. Top mechanism, uncatalyzed or Lewis acid catalysis; bottom mechanism, Brønsted acid catalysis.

In the absence of catalyst, the enthalpy of activation of the dehydration of the oxanorbornene derivative is 60 kcal/mol and is associated with the breaking of the C-O bridge. When the reaction is carried out in Sn-, Zr-, or Ti-BEA with unhydrolyzed active sites, the respective barriers decrease to 31, 30, and 36 kcal/mol, respectively. These energy barriers seem to track the partial charges of the metal centers, with Ti being the less positively charged of the three. In Sn- and Zr-BEA with hydrolyzed active sites we can have coordination of the cycloadduct either to the Lewis-acidic metal center or to the moderately Brønsted-acidic silanol group. In the former case, the C-O cleavage intrinsic barriers drop further to 25 and 24 kcal/mol for Sn- and Zr-BEA, respectively, and the reaction proceeds through the formation of an alkoxy intermediate species. Figures 5.5a and 5.5b show the coordination geometries of the cycloadduct to the metal center of the closed and open sites of Sn-BEA, respectively. We see that they are very similar, other than the distance between the O atom of the cycloadduct and the



Figure 5.4. Enthalpy profiles for the Diels-Alder aromatization of DMF and ethylene to *p*-xylene for the a) unhydrolyzed ("closed") and b) hydrolyzed ("open") active sites. Values marking transition states indicate intrinsic reaction barriers of corresponding elementary steps and are colored to match the legend. Homogeneous, uncatalyzed reactions calculated at the M06-2X/6-311G(d,p) theory level.



Figure 5.5. Binding geometries of the Diels-Alder cycloadduct at the Sn-BEA a) "closed" and b) "open" active sites. In both cases coordination is via the bridge O atom of the cycloadduct. Notice the difference in the metal atom-O atom distance, suggesting much stronger interaction of the cycloadduct with the open active site.

Sn atom being 0.5 Å shorter at the open active site. As a result, the cycloadduct and the alkoxy intermediate that result from the opening of the C-O bridge bind more strongly to the open site than the closed one, by 10-15 kcal/mol. Although the partial charges of the metal centers seem to track the relative activities of Sn-, Zr- and Ti-BEA, they still cannot explain the differences in activity between the closed and open sites, as the hydrolysis of the closed sites has no effect on the population of the metal orbitals.

When the cycloadduct coordinates to the silanol group of an open site, the breaking of the C-O bridge is accompanied by proton transfer from the silanol to the O atom of the bridge, evoking enforced general acid catalysis. However, the resulting

protonated intermediate is very unstable relative to the alkoxy intermediate mentioned earlier. The corresponding intrinsic enthalpy barriers are respectively 29 and 30 kcal/mol for Sn- and Zr-BEA with open sites. These are practically the same as those found for the closed active sites and about 5 kcal/mol higher than the corresponding barriers across the pathways involving coordination to the Lewis acid center alone.

To better understand the acid strength of these solid acids and their effect on the oxanorbornene C-O bond, we have analyzed the electron density and the Laplacian of the electron density of the coordinated cycloadduct using Bader's theory. In Figure 5.6, we plot the values of the density and of its Laplacian at the bond critical point (BCP) of the C-O bond. The density at the BCP correlates well with the cleavage barrier. Adsorption onto the open active sites results in a greater depletion of the C-O bond density than to the closed active site, and thus a lower cleavage barrier. The negative of the Laplacian is positive, indicating a concentration of charge at the BCP representative of a covalent-type bond [143], and demonstrates a similar linear trend.

5.3.3 Confinement and entropy

Confinement and the concomitant entropic changes can influence the Gibbs free energy changes along a catalytic pathway. Upon adsorption, it is unknown how much freedom a guest molecule has to move inside the pore. We have considered both immobile and mobile adsorbates. In the latter case, in particular, any one of the guest molecules has been allowed to move freely in either one or two dimensions; and for the calculation of the corresponding translational entropy we have assumed either a length of 800 pm or a molecular surface area of $800 \times 800 \text{ pm}^2$, characteristic of the BEA framework pore size [97].


Figure 5.6. Enthalpy of activation of cycloadduct C-O bridge cleavage plotted against the value of the electron density and the value of the negative of the Laplacian of the electron density at the (3,-1) bond critical point (BCP) of the C-O bond.

Calculated free energy profiles of the cycloaddition are shown in Figure 5.7 for Sn, Zr and Ti-BEA, both for closed and open sites; profiles for the entire tandem scheme are shown in Figures D.2, D.3, and D.4 of Appendix D. The assumption of immobile adsorbates (Figure 5.7a) leads to the largest entropic losses and neither DMF nor the DMF-ethylene interacting complex adsorb favorably in the zeolite. In this case one should expect very low DMF coverages. The DA apparent free energy barriers, ΔG^{\ddagger} , are in the range of 41-46 kcal/mol, namely 0-5 kcal/mol higher than the uncatalyzed reaction in heptane ($\Delta G^{\ddagger}=41$ kcal/mol at 250°C). For mobile adsorbates with one translational degree of freedom in the pore (1D), DMF binds only to the open-Sn- and open-Zr active sites, albeit weakly, whereas the complex of the two addends is unstable



Figure 5.7. Free energy profiles for the Diels-Alder cycloaddition of DMF and ethylene in different catalysts for a) immobile adsorbates, b) mobile adsorbates, free to undergo translational motion in one dimension, and c) mobile adsorbates, free to undergo translational motion in two dimensions. Values marking the transition states indicate free energy barriers with respect to isolated reactants or to adsorbed DMF, whichever is lower in energy. Homogeneous, uncatalyzed reaction calculated at the M06-2X/6-311G(d,p) theory level.

in all zeolites tested (Figure 5.7b). In the 1D case, the apparent Gibbs free energy of DA activation is *ca*. 36 kcal/mol for open-Zr, 38 kcal/mol for open-Sn, and *ca*. 40 kcal/mol for the rest. Therefore, we see a 1-5 kcal/mol acceleration, at the most. Allowing for two translational degrees of freedom in the pore (2D) predicts stronger DMF binding in all the systems Figure 5.7c. However, the DMF-ethylene complex remains unstable, although less so in open-Sn and open-Zr. In the 2D case, the Gibbs free energies of activation are in the range of 36-38 kcal/mol, namely a 3-5 kcal/mol drop relative to the uncatalyzed reaction. In the above discussion, the apparent activation energies are transition states referenced to either isolated reactants or adsorbed DMF, whichever is lower in energy [176-178]. To see this, one should consider the rate expression $v_{DA}=k_{DA}K_{DMF}K_{eth}[DMF][eth]C_0/(1+K_{DMF}[DMF])$, which describes the rate along the heterogeneous DA pathway for unstable DMF-ethylene interacting complexes, a good approximation according to the free energy profiles of Figure 5.7. In this expression,

 k_{DA} is the intrinsic DA rate constant on the catalyst, K_{DMF} is the DMF adsorption equilibrium constant, K_{eth} is the equilibrium constant for the formation of the ethylene-DMF-active site complex that follows DMF adsorption, and C_0 is the concentration of active sites. For unfavorable DMF binding, one can further simplify to $v_{DA} \cong k_{DA}K_{DMF}K_{eth}[DMF][eth]C_0$ because $K_{DMF}[DMF]\ll 1$, whereas for favorable DMF binding $K_{DMF}[DMF]\gg 1$ and $v_{DA}\cong k_{DA}K_{eth}[eth]C_0$.

Thus, depending on the entropic losses, the free energy profiles suggest transition from no catalysis of the Diels-Alder for immobile adsorbates in the pore, to modest catalysis in the 1D (only Zr and Sn) or 2D cases by *ca*. 1-5 kcal/mol. We should note that the latter two cases do not seem in line with the nonlinear behavior of the rate of the tandem scheme as a function of the acid site concentration. Chang *et al.* [31] have reported that the rate varies linearly at small acid site concentrations and that it reaches a plateau at high ones, suggesting a switch in the rate-limiting pathway – to one that is unaffected by the presence of a catalyst. For a more complete picture of the overall kinetics and of the various contributions to the overall rate, we have employed microkinetic modelling and investigated all three cases of adsorbate mobility. We compare the predicted *p*-xylene formation rates with experimental data [31] and obtain apparent activation energies at four different catalyst loadings, which we compare with experimental values obtained by Yu *et al* [32].

5.3.4 Hydrolysis of 2,5-dimethylfuran

Before we delve into the micro-kinetic model, however, we shall digress to discuss briefly the most dominant, undesired side-reaction: the hydrolysis of DMF to 2,5-hexanedione, shown in Figure 5.8. Experimentally, 2,5-hexanedione is observed in the products, demonstrating that Sn-, Zr- and Ti-BEA do not completely eliminate it.



Figure 5.8. Reaction mechanism for the hydrolysis of DMF.

Water for this reaction can either be found residually in the experimental system, or is produced through the dehydration of oxanorbornene. Brønsted acids catalyze the hydrolysis by protonating the β -C of DMF, before a water molecule nucleophilically attacks the α -C [118]. Such an acidic proton, however, is not available in the zeotypic Lewis acids with unhydrolyzed active sites, and our calculations have yielded barriers of 51 kcal/mol, suggesting no catalysis by the Lewis-acidic metal center. In fact, catalysis of the hydrolysis is possible only at open active sites *and only with the involvement* of the modestly Brønsted-acidic Si-OH group, requiring a barrier of about 35 kcal/mol. So, the presence of 2,5-hexedione among the products indicates, albeit indirectly, the presence of open active sites or of defect sites.

5.3.5 Microkinetic modelling

Given the error inherent in electronic structure calculations of systems so complex as ours, our intent in employing microkinetic modelling is not so much to test the ability of different functionals to predict the kinetics as to interpret the experimental data using the best available estimates of the relevant kinetic parameters, in order to predict rates that match the experimental ones as closely as possible. We have run the microkinetic model for two sets of kinetic parameters that differ in the theory level used to model the homogeneous Diels-Alder reaction. In the first set, the kinetics of the homogeneous DA was treated at the M06-2X/6-311G(2df,p) level, *viz.*, at the same level as the high-theory layer of the ONIOM model. In the second set, the homogeneous DA was treated at the CBS-QB3 level. In the latter, the thermodynamic consistency of the microkinetic model was ensured by adjusting the cycloadduct adsorption/desorption equilibrium constant – a fast step that has no effect on the overall reaction rate (Tables D.2 and D.3 of Appendix D). Of the two sets of parameters, the first (M06-2X/6-311G(2df,p)) underestimates the rate of *p*-xylene formation by a factor of 10, whereas the second overestimates the rate by only a factor of 2, matching the experimental data much closer. In the following, we present and discuss results obtained from the latter. The kinetic analyses based on the first set of parameters is presented in Appendix D, Tables D.4 and D.5, and Figures D.5 and D.6. We should stress that both sets of parameters lead to the same qualitative conclusions, the differences in the predicted rates notwithstanding.

In Figure 5.9, we plot the *p*-xylene production rate against the acid site concentration. When the adsorbates are treated as immobile (Figure 5.9a), only open-Sn-BEA and open-Zr-BEA show activity. Sn-BEA is also predicted to be less active than Zr-BEA and does not reach a plateau over the range of acid site concentrations considered, for reasons that become clear from sensitivity analysis of the rate (*vide infra*). In Zr-BEA, the rate increases up to an acid site concentration of *ca*. 2 mM, before plateauing at a rate of *ca*. 500 mM/h, which is in satisfactory agreement with the experimental value of *ca*. 200 mM/h, considering that at 250°C a factor of two can be traced to a free energy error of about 1 kcal/mol [31]. When we assume mobile species



Figure 5.9. Microkinetic model predicted rates of p-xylene production as a function of acid site concentration, using the CBS-QB3 theory level parameterization for the homogeneous Diels-Alder reaction. a) Immobile adsorbates. b) Mobile adsorbates free to undergo translational motion in one dimension.
c) Mobile adsorbates free to undergo translational motion in two dimensions. Simulations run at experimental conditions, 250 °C and 37 atm.

with one or two translational degrees of freedom (Figures 5.9b and 5.9c), the activity of open-Sn-BEA becomes comparable to that of open-Zr; we also see clear plateauing of the rate at high acid site concentrations, in contrast to immobile adsorbates. Quite interestingly, we see increased closed-Zr-BEA activity if we allow for adsorbate mobility, but still less than open-Zr and open-Sn. The rest of the tested catalytic systems, closed-Sn, and closed-Ti, are inactive on account of the significantly higher dehydration barriers, irrespective of adsorbate mobility (Figures D.2, D.3, and D.4 in Appendix D). Sensitivity analysis of the computed rates (Figure 5.10), in conjunction with the free energy profiles, can help us apprehend the reasons behind the rate behavior. The sensitivity analysis for the five active systems (open-Sn and open-Zr and closed-Zr, with immobile or mobile adsorbates) at four acid site concentrations, 0.1, 1, 5 and 12 mM, reveals that at small acid concentrations the rate-limiting step is the dehydration of the cycloadduct, presumably because there are not enough active sites to bind and



Figure 5.10. Sensitivity analysis for the formation of p-xylene from DMF and ethylene in open-Sn-BEA with a) immobile adsorbates, b) adsorbates with 1D translation in the pores, and c) adsorbates with 2D translation in the pores; open-Zr-BEA with d) immobile adsorbates, e) adsorbates with 1D translation in the pores, and f) adsorbates with 2D translation in the pores; and closed-Zr-BEA with g) immobile adsorbates, h) adsorbates with 1D translation in the pores, and i) adsorbates with 2D translation in the pores. For all systems considered, the heterogeneous Diels-Alder NSC was less than 0.01 and thereby has been omitted from the figures for clarity. The CBS-QB3 theory level parameterization has been used for the kinetics of the homogeneous Diels-Alder reaction.

turn the homogeneously produced cycloadduct into p-xylene, despite the fact that the heterogeneous dehydration requires much less activation than the homogeneous DA, according to the computed energy profiles. This is in line with the linear behavior seen in Figure 5.9 and with earlier studies of the reaction on Brønsted acidic zeolites. At high acid concentrations, the rate is not limited by the availability of active sites but rather by how fast cycloadduct can be produced homogeneously. Thereby, the rate approaches a maximum, which for the most part is determined by the homogeneous Diels-Alder, invariably for all the catalytic models tested. Quite remarkably, the heterogeneous DA pathway makes almost no contribution to the rate, as the corresponding normalized sensitivity coefficients (NSC) are less than 0.01 (not shown in Figure 5.10). Comparing Figures 5.10a and 5.10d, respectively for open-Sn and open-Zr with immobile adsorbates, we see that in open-Sn the heterogeneous dehydration pathway contributions to the rate (green and red bars) are substantial even at 12 mM, which explains why the rate reaches its maximum value slower than in open-Zr. In open-Sn with mobile adsorbates (Figures 5.10b and 5.10c), on the other hand, the contribution of the dehydration pathway is substantially diminished at concentrations higher than 5 mM and thereby we see activity very close to that of open-Zr, at all acid concentrations. These results are in agreement with experiment, and qualitatively independent of the theoretical model used for the parameterization of the homogeneous Diels-Alder reaction (cf. Figure 5.10 and Figure D.6 in Appendix D). Closed-Zr is more active than the rest of the closed-active-site systems because of faster dehydration. In the best case scenario for all catalysts tested – translational entropy of adsorbates in two dimensions - the cycloadduct bridge C-O cleavage free energy barrier is ca. 27 kcal/mol in closed-Zr, compared with *ca*. 36 kcal/mol in closed-Sn and 40 kcal/mol in closed-Ti. Yet, this barrier is still higher than those in open-Sn and open-Zr, around 20 kcal/mol in both (Figures D.2, D.3, and D.4 in Appendix D). As a result, the rate of *p*-xylene formation is determined by the dehydration reaction even at acid site concentrations as high as 12 mM (Figures 5.10g, 5.10h and 5.10i), without reaching a plateau.

In Figure 5.11, we plot the DMF conversion over time. For the zeolitic Lewis acids that were deemed inactive, it is clear that the lack of activity arises from failure to convert DMF and is not due to undesired products, *e.g.* 2,5-hexanedione. When adsorbates are treated as immobile (Figure 5.11a), the DMF conversion over time is in very good agreement with experiment for open-Sn and open-Zr. When mobile adsorbates are considered (Figures 5.11b and 5.11c), we see an increase in the DMF conversion in closed-site Zr-BEA, which is consistent with the rate increase observed in Figures 5.9b and 5.9c.

In Figure 5.12, we plot the product formation as a function of DMF conversion in open-Sn-BEA and open-Zr-BEA. Both immobile and mobile adsorbates produced the same results. For open-Sn, (Figure 5.12a), there is satisfactory agreement for both the *p*-xylene and 2,5-hexanedione yields. At *ca*. 60% DMF conversion, the 2,5hexanedione yield reaches a maximum before beginning to decrease, as the model shows that equilibrium converts it back to DMF as the latter is consumed. The comparison of open-Zr (Figure 5.12b) is also in satisfactory agreement with experiments. The 2,5-hexanedione production is predicted to be lower than in Sn-BEA, in qualitative agreement with experiments, and does not reach its maximum until *ca*. 90% conversion of DMF.



Figure 5.11. Microkinetic model predicted DMF conversion as a function of time, using the CBS-QB3 theory level parameterization for the homogeneous Diels-Alder reaction for a) immobile adsorbates, b) mobile adsorbates free to undergo translational motion in one dimension, and c) mobile adsorbates free to undergo translational motion in two dimensions. Simulations run at experimental conditions, 250 °C and 37 atm.



Figure 5.12. Microkinetic model predicted *p*-xylene (pX) and 2,5-hexanedione (HDI) yields as a function of DMF conversion, using the CBS-QB3 theory level parameterization for the homogeneous Diels-Alder reaction in a) open-Sn-BEA and b) open-Zr-BEA.

Using the MKM, we have also obtained apparent activation energies at four different acid site concentrations (0.1, 1.0, 5.0 and 12.0 mM). In Table 5.2, we compare the computed apparent activation with the experimental ones obtained by Yu et al [32]. For the Lewis acids that showed the greatest activity (open active sites), the apparent activation energies at low acid site concentrations are in the 13-17 kcal/mol range before increasing to *ca*. 21 kcal/mol as the catalyst loading increases. This increase in apparent activation energy is in line with the predicted change in rate-determining step, from the fast heterogeneous dehydration at low acid concentrations to the relatively slow, uncatalyzed homogeneous Diels-Alder cycloaddition at high acid concentrations. The closed-Zr, which showed lower activity than either of the systems with open active sites, shows the opposite trend, namely a decrease in apparent activation energy, from ca. 20 to 17 kcal/mol as the acid site concentration increases. The sensitivity analysis for closed-Zr indicates that both homogeneous Diels-Alder cycloaddition and heterogeneous dehydration are active pathways at the higher catalyst loading, suggesting that a single pathway cannot explain the observed barrier. The agreement with experiment is overall quite satisfactory. More specifically, the experimental values of 15.5 and 16.3 kcal/mol for open-Sn and open-Zr, respectively, are in good agreement with the computed values at low acid site concentrations and they also indicate that the reactor was operated in the dehydration-limited regime [32].

Table 5.2. Experimental and computed apparent activation energies of the active catalytic systems for immobile adsorbates and for adsorbates allowed to translate freely in one and two dimensions. Microkinetic model run for 15% DMF in 100 mL *n*-heptane with 200 psi ethylene at 250°C, 550 psi, and for 50 minutes with the indicated catalyst loading.

Ea (kcal/mol)	Immobile Adsorbates	Adsorbates – 1D Translation			Adsorbates – 2D Translation		
Acid Site Conc. (mM)	Zr-BEA "Open"	Sn-BEA "Open"	Zr-BEA "Open"	Zr-BEA "Closed"	Sn-BEA "Open"	Zr-BEA "Open"	Zr-BEA "Closed"
<i>Exp.</i> $(0.1 g)$	16.3	15.5	16.3	16.3	15.5	16.3	16.3
0.1	13.0	14.8	16.7	19.7	15.2	16.7	20.9
1.0	17.4	18.4	18.4	19.6	18.7	18.5	20.6
5.0	20.2	20.3	20.4	17.4	20.4	20.4	17.6
12.0	20.9	20.7	20.8	16.5	20.7	20.8	16.5

5.4 Discussion

The computed enthalpy profiles do not suggest catalysis of the Diels-Alder of DMF and ethylene since the barriers are consistently in the 23-25 kcal/mol range, compared to the 24 kcal/mol barrier of the unanalyzed reaction in heptane solvent. Thus, from an electronic point of view, the Lewis acid centers seem unable to induce sufficient charge transfer to promote inverse electron demand cycloaddition when the furan is coordinated to the active site. Confinement and the attendant entropic phenomena turn out to have a modest effect on the Diels-Alder reaction. For immobile adsorbates, the free energy profile barriers indicate no catalysis by either one of the zeotypic Lewis acids tested in this work. If we allow for adsorbates with one or two translational degrees of freedom, then the Diels-Alder apparent free energies drop by 1-5 kcal/mol relative to the uncatalyzed reaction. Although we have no way of ascertaining the translational freedom of the DA addends in the pores, this modest decrease suggests minor catalysis, which should be solely attributed to entropic effects. Notwithstanding this uncertainty,

the microkinetic model and the accompanying sensitivity analyses reveal unequivocally that the heterogeneous DA pathway has negligible contribution to the overall rate of the tandem Diels-Alder aromatization. Only the homogeneous DA pathway controls the rate of the reaction, and then only at high acid site concentrations. Comparing the rates of the homogeneous and heterogeneous DA reactions, we see that, depending on the system, the latter is slower by 3-7 orders of magnitude when compared to the homogeneous reaction at the CBS-QB3 level (Table D.6) or 2-6 orders of magnitude when compared to the homogeneous reaction at the M06-2X/6-311G(2df,p) level (Table D.7) – the combined effect of the modest drop in activation energy, the rather weak binding of DMF in some systems, and the unstable nature of the interacting complex of the two addends due to entropic losses.

If we consider the CBS-QB3 parameterization of the homogeneous DA reaction, the above order of magnitude differences suggest that, even for the best case scenarios, an *additional* decrease in the heterogeneous DA activation energy by *at least* 8 kcal/mol would be required before it became catalytically relevant. For example, in the cases of open-Sn, open-Zr and closed Zr, the heterogeneous DA activation energies would have to be further reduced by *ca*. 12, 14 and 14 kcal/mol, respectively, at 12 mM catalyst loading. These figures should be reduced by 4 kcal/mol if we consider the M06-2X/6-311G(2df,p) parameterization of the homogeneous DA, since at this theory level the homogeneous DA reaction is predicted to be slower by that amount compared with CBS-QB3.

Our calculations show that the open sites are catalytically more active than the closed ones. Although there is the potential for Brønsted acidity within the zeolites with open sites (from the formation of silanol groups), the calculations predict higher activity

by the Lewis-acidic metal centers – especially for Zr-BEA. This is important for two reasons. First, the quite remarkable finding that Lewis acids can catalyze dehydration reactions opens the possibility of a wider range of catalysts, beyond Brønsted acids, capable of catalyzing the dehydrative aromatization of Diels-Alder products between functionalized furans and olefins. Second, we show for the first time that the silanol groups of the open sites can effect Brønsted acid catalysis, and are in fact solely responsible for the hydrolysis of furans. Thus, elimination of undesired side-reactions that require Brønsted acid catalysis, including side reactions that can cause catalyst coking, might require the design of catalysts that do not possess Brønsted acidity.

Finally, and in stark contrast to what Chang *et al.* have reported [31], our calculations predict that Ti-BEA (with unhydrolyzed Lewis acid sites) is a very weak Lewis acid and practically inactive (Figure 5.9), as we found no catalysis of the dehydration of the Diels-Alder cycloadduct. (As we noted earlier, our conclusions hold irrespective of the theory level used in the small (high-level) layer. Single-point energy calculations at the M06-2X/Def2TZVP theory level for the small layer on pre-optimized structures did not show a significant effect on the calculated free energy profiles (see Table D.1 of Appendix D). We believe that this strongly suggests the presence of Brønsted-acidic defect sites in the Ti-BEA tested by Chang *et al.* Our finding is in agreement with a recent report by Pacheco *et al.* [29], who found that the Diels-Alder aromatization of methyl 5-(methoxymethyl)furan-2-carboxylate over Ti-BEA is much slower than over Sn-BEA and Zr-BEA [29]. Unlike Sn-BEA, the active site structure in Ti-BEA is not fully understood, owing to a lack of suitable characterization techniques [179].

5.5 Conclusions

We have employed electronic structure calculations and microkinetic modelling to investigate the Diels-Alder aromatization of 2,5-dimethylfuran and ethylene to *p*xylene over the Lewis-acidic zeotypes Sn-, Zr- and Ti-BEA. We have been motivated by the fact that, while the published experimental work has made it clear that these Lewis acids can catalyze the dehydration of the Diels-Alder product of 2,5dimethylfuran and ethylene, the kinetic studies have not been able to elucidate whether these same Lewis acids can also catalyze the Diels-Alder step itself.

The present study has shown that there is only minor catalysis of the Diels-Alder, which should be solely attributed to confinement (*i.e.* entropic) phenomena that vary according to the translational freedom allowed to the species inside the zeolite; the Diels-Alder free energy barriers drop by a modest 1-5 kcal/mol as we increase the translational degrees of freedom of the adsorbates in the pores. However, sensitivity analysis of the MKM-predicted rates shows that the heterogeneous Diels-Alder pathways do not contribute to the overall rate even if we allow for mobile adsorbates in the zeolite. In addition, the same analysis reveals that the rate of *p*-xylene formation is limited by the homogeneous cycloaddition at high acid site concentrations.

Our calculations have also shown that only the partially hydrolyzed ("open") Lewis acid sites are catalytically active and that the silanol group of the open sites is moderately Brønsted acidic and, in fact, catalytically responsible for the hydrolysis of the furan.

Of the three zeotypic Lewis acids tested in this work, Zr-BEA and Sn-BEA have very similar activities, in agreement with experiment, while Ti-BEA is found to be quite inactive, which leads us to suggest that the Ti-BEA catalytic activity recently reported for the formation of *p*-xylene from dimethylfuran and ethylene was likely due to defect sites possessing Brønsted acidity.

5.6 Acknowledgements

This material has been adapted with permission from Patet, R.E., Fan, W., Vlachos, D.G., and Caratzoulas, S. Tandem Diels-Alder of dimethylfuran and ethylene and dehydration to para-xylene catalyzed by zeotypic Lewis acids. *ChemCatChem* **2017**, D.O.I. 10.1002/cctc.201601584. I would like to thank the co-authors of this work, Prof. Wei Fan for his experimental insights, and Prof. Dionisios G. Vlachos and Dr. Stavros Caratzoulas for their contributions and insights.

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Chapter 6

CHARACTERIZATION OF THE AROMATIZATION OF OXYGENATED FURANS BY FRAMEWORK ZINC IN ZEOLITES USING FIRST PRINCIPLES CALCULATIONS

6.1 Introduction

Demand for bio-based alternatives to the conventional polyethylene terephthalate (PET) plastics used in applications such as plastic bottles continues to rise as consumers seek more environmentally conscious options [10, 180]. The market size for bio-based PET was a sizable 850,000 tons in 2015, representing slightly over 1% of total PET production, and is projected to grow three-fold in the next decade [10, 180]. Of the bio-based PET being produced, only the *ca.* 30% of its content from ethylene glycol (MEG) can be claimed as truly bio-derived, with the remaining *ca.* 70% derived from petroleum-based terephthalic acid (PTA) [10, 180].

Extensive research has targeted renewable routes to PTA (Figure 6.1) to provide the market with 100% bio-based PET products, with promising results coming from a pathway involving the aromatization of furans with ethylene [14-17, 19-21, 25, 27, 29-31, 33, 112, 118, 126-128, 150, 181, 182]. The highest yields to aromatics have been achieved using 2,5-dimethylfuran (DMF) to produce *p*-xylene over solid acid zeolites [21, 25]. Under the same reaction conditions, furans without the methyl groups on both the 2 and 5 carbons (*e.g.* furan and 2-methylfuran) or with oxygenated side groups (*e.g.* 2,5-furandicarboxylic acid) are active, but with significant decreases in aromatic yield



Figure 6.1. Reaction pathways for the production of terephthalic acid from hydroxymethylfurfural

and selectivity [14, 127, 128]. Despite the successes of *p*-xylene production, DMF synthesis from biomass requires hydrodeoxygenation of hydroxymethylfurfural (HMF) over expensive metal catalysts and must be re-oxygenated to form the final PET product [23, 24].

Recent discoveries with framework-substituted Lewis acid zeolites have demonstrated an increase in the selectivity and yield to aromatics when starting from oxygenated furans [29, 30, 33]. Reactions run by Pacheco and Davis with Lewis acidic Sn- and Zr-BEA materials demonstrated considerable increases in aromatic selectivity from oxygenated furans, as compared to Brønsted acidic zeolites [29, 30]. This success prompted investigation by Orazov and Davis into another Lewis acid zeolite (CIT-6) containing framework-substituted Zn [33]. With this material, aromatic selectivities as high as 62% and 36% were achieved from methyl 5-(methoxymethyl)furan-2carboxylate (MMFC) 2,5-furandicarboxylate and (DMFDC), respectively. Interestingly, differences in the selectivities to aromatic by as much as 30% were seen depending on the preparation methods of the materials.

Orazov and Davis propose a possible explanation for the differences in product selectivities based on their characterization of the active site using IR studies of adsorbed pyridine and deuterated acetonitrile (CD₃CN) [33]. Adsorbed pyridine showed no peak at *ca.* 1550 cm⁻¹, characteristically attributed to strong Brønsted acid sites in zeolites. Deuterated acetonitrile showed two peaks in the IR spectra, at 2311 and 2290 cm⁻¹, theorized to be representative of two distinct Lewis acid sites in these materials. The peak at 2311 cm⁻¹ is similar to adsorption peaks found in Sn and Zr-containing zeolites (*ca.* 2309-2315 cm⁻¹), and the peak at 2290 cm⁻¹ is similar to Li-exchanged Sn-BEA (*ca.* 2292 cm⁻¹) [173, 183-185]. For the CIT-6 material, changes in the synthesis resulted in changes in the site distribution, as measured by the ratio of these two peaks in the CD₃CN spectra. Li⁺ exchange in a moderately basic solvent generated a material possessing primarily the 2290 cm⁻¹ band, while the neutral exchange of N(CH₃)₄Cl and calcination generated a material possessing primarily the 2312 cm⁻¹ band. The observed differences in the aromatic selectivity are attributed to differences in the abundance of these two theorized active sites.

Possible structures of these two distinct Lewis acid sites have been proposed (Figure 6.2) [33]. The incorporation of Zn(II) into a zeolite framework in place of a Si(IV) creates a zeolite framework with -2 charge. The three proposed structures differ in the identity of the pore cations used to neutralized the charge; two protons (Z_0), one proton and a counter-cation (Z_1), or two counter-cations (Z_2). From this experimental study, little is known about the nature of the Zn in these materials. However, the formation of adjacent silanols to the framework Zn atom when protons are pore cations (Z_0 and Z_1), is thought to break the formal bonding of the Zn to the adjacent framework oxygen, changing its electronic properties and strength as a Lewis site.

To our knowledge, no computational studies have examined the active site of framework-substituted Zn zeolites. In this study, we use density functional theory



Figure 6.2. Proposed active site structures of framework-substituted Zn-BEA [33].

calculations to construct models of the proposed Z_0 and Z_2 active sites in zeolite BEA. We examine the bonding properties of the framework Zn atom using NBO and Bader analyses, as well as the adsorption of deuterated acetonitrile and pyridine as probe molecules. Finally, we examine the reaction profiles for the aromatization of MMFC and DMFDC. We conclude that differences in adsorption and reactivity arise from blocking of the Zn atom by the larger Li⁺ cations in the Z₂ structure, rather than differences in the nature of the bonds of the framework Zn. Qualitative experimental observations of decreased rates from Z₂ sites and DMFDC, as compared to Z₀ and MMFC, respectively, are supported by differences in the reaction barriers of the calculated profiles.

6.2 Computational Methods

CIT-6 is a zeolitic material with a BEA morphology containing 9 unique tetrahedral substituent positions, which can be grouped into three distinct classes (T1-T4, T5-T6, and T7-T9) [76]. Zn atom substitution energies are similar within the different classes of substituents (Table E.1 of the Appendix E), and therefore we have selected T5 and T7 substituents to investigate two of these classes. The T5 position is only accessible through one pore of the BEA zeolite, while the T7 position is located at

the intersection of two pores. We, therefore, constructed two models for the T7 substituent position: one with the "top" pore defined (corresponding to the same pore with access to the T5 substituent) and a second with the "side" pore defined.

Zeolite pore models were constructed following the procedure outlined by Migues, *et al.* [186]. In brief, a portion of the zeolite active site and surrounding pore was cut out from the extended zeolite framework and saturated with hydrogen atoms [76]. Of the proposed active sites in Figure 6.2, we have chosen the Z_0 and Z_2 (M⁺ = Li^+). These structures were chosen over the Z_1 site to reduce the combinatorial possibilities of the active site while still examining the extrema of the proposed structures. Inside this pore, geometry optimizations of co-adsorbed DMFDC and ethylene in 2-4 different orientations were run at a theory level with a minimal basis set (M06-2X/3-21G). Upon completion of the optimization, only the framework atoms within 5 Å of the Zn substituent atom, the counter-cations (H⁺ or Li⁺), or the atoms of the co-adsorbed DMFDC and ethylene were retained for the final model. Hydrogen atoms were added to any unsaturated silicon or oxygen atoms at the extremity of the model, with all saturating hydrogens and oxygens bonded to a saturating hydrogen frozen geometrically. The resulting T5 "top" model has a stoichiometry of Zn[H₂/Li₂]Si₄₄O₈₈H₅₄, T7 "top" model has a stoichiometry of Zn[H₂/Li₂]Si₄₇O₈₈H₆₀, and T7 "side" model has a stoichiometry of Zn[H₂/Li₂]Si₃₉O₈₁H₅₄, as shown in Figure 6.3.

Subsequent calculations were run in these zeolite models at the M06-2X/6-31G(d,p) theory level using the Gaussian 09 program [80]. Adsorption energies have been corrected for the basis set superposition error (BSSE) using the counterpoise method. Thermal corrections to the energies of adsorbed states have been computed within the quasi-rigid rotor harmonic approximation (q-RRHO), and assuming mobile



Figure 6.3. Models of Zn-BEA with (a) T5 substituent with "top" pore, (b) T7 substituent with "top" pore, and (c) T7 substituent with "side" pore. Zn atoms are represented as orange, Si as grey, O as red, and H as white. Atoms located above the substituted Zn atom (from shown perspective) have been shown as wireframes for clarity.

adsorbates in two-dimensional space with a characteristic area of $800 \times 800 \text{ pm}^2$ [71, 89, 126, 127]. Ground and transition states were characterized by frequency analysis and all transition states were further validated by intrinsic reaction coordinate (IRC) calculations [140]. Bader analysis of the systems was performed using the AIM2000 software [141, 187, 188].

6.3 **Results and Discussion**

6.3.1 Active site bonding properties

The images in Figure 6.4 depict bonding structures obtained from NBO analysis of the Z_0 and Z_2 active sites with Zn in the T5 or T7 position. For the Z_0 active sites (Figures 6.4(a)-(c)), the Zn atom is covalently bonded to a single framework oxygen atom and ionically bonded to the other three nearest-neighbor framework oxygen atoms, irrespective of the Zn position. In all three active site models, the protons are on two of



Figure 6.4. Local bonding structures for six active site models, obtained from NBO analysis: (a) T5, "top", Z₀; (b) T7, "top", Z₀; (c) T7, "side", Z₀; (d) T5, "top", Z₂; (e) T7, "top", Z₂; and (f) T7, "side", Z₂. Atoms beyond the Siatoms immediately neighboring the Zn atom have been removed from the images for clarity.

the three oxygen atoms that are ionically bonded to Zn. For the Z_2 active sites with two Li⁺ countercations, (Figures 6.4(d)-(f)), the NBO analysis shows that the Zn atom is ionically bonded to all four nearest-neighbor O atoms for the T5 and T7 "top" sites, and covalently bonded to a single O in the T7 "side" site. In the systems where no covalent bond is calculated between Zn and a neighboring O, a small amount of non-Lewis, lone valency electron density is predicted on the Zn atom. This non-Lewis electron density is indicative of hypovalent atom, lacking its full valency of electrons [175]. This empty valence orbital is consistent with Zn in the +2 oxidation state.

The nature of these bonds has been further studied by Bader analysis. For both the Z_0 and Z_2 active sites, the negative of the Laplacian of the density takes on negative values at the bond critical points (BCP) of the Zn-O bonds, indicating ionic-type bonding between Zn and the O atoms (Table 6.1). Moreover, the electron density around all Zn-O bonds is very small, in the 0.07-0.11 a.u. range. There are no significant differences in the density or Laplacian of the density at the BCPs of the Zn-O bonds, whether or not a formal covalent bond is predicted by NBO analysis.

The NBO and Bader analyses provide, in large measure, a consistent story on the nature of bonding at the active site, notwithstanding the single covalent Zn-O bond predicted by NBO for four of the systems which is not predicted by Bader. To eliminate basis set effects, we picked the T5 "top" site and repeated the NBO and Bader analyses using structures optimized with the 6-311G(2df,p) and 6-311++G(3df,3pd) basis sets for all atoms shown in Figure 6.4. We observed no differences upon comparison with the results obtained at the M06-2X/6-31G(d,p) level (Table E.2 of Appendix E).

The mostly ionic nature of the bonding of Zn(II) at the active site does not agree with that proposed by Orazov and Davis (Figure 6.2) [33]. The ionic nature of the Zn atom in the framework could help support one experimental observation, however: isomerization reactions run in water resulted in irrecoverable loss in activity and decrease in Zn content of the zeolite, possibly due to leaching of the Zn(II) cations from the framework [33]. A Zn(II) atom with weak ionic bonds to the zeolite framework could be expected to easily leach from the zeolite into water.

6.3.2 Adsorption characterization

Pyridine, commonly used to probe for Brønsted acidity in zeolites, and deuterated acetonitrile used to probe Lewis acidity, offer insight into the nature of the

	Z ₀			Z_2		
ρ (a.u.)	Т5 "Тор"	Т7 "Тор"	T7 "Side"	Т5 "Тор"	Т7 "Тор"	T7 "Side"
Zn-O4	0.11	0.11	0.11	0.09	0.08	0.07
Zn-05	0.06	0.07	0.06	0.06	0.09	0.09
Zn-06	0.07	0.07	0.07	0.09	0.09	0.09
Zn-07	0.11	0.11	0.12	0.11	0.11	0.11
05-H2/Li2	0.34	0.33	0.34	0.03	0.04	0.04
06-H3/Li3	0.35	0.35	0.35	0.04	0.04	0.04
$-\frac{1}{4}\nabla^{2}(\rho)$ (a.u.)						
Zn-O4	-0.14	-0.13	-0.13	-0.11	-0.08	-0.08
Zn-05	-0.07	-0.08	-0.07	-0.07	-0.11	-0.11
Zn-06	-0.08	-0.08	-0.08	-0.10	-0.10	-0.10
Zn-07	-0.13	-0.14	-0.15	-0.13	-0.13	-0.14
O5-H2/Li2	0.51	0.51	0.51	-0.06	-0.07	-0.08
06-H3/Li3	0.51	0.53	0.52	-0.09	-0.09	-0.09

Table 6.1. Bader analysis of bond critical points of the local active site. Atom numbering scheme corresponds to that found in Figure 6.4.

active sites in these zeolites [33]. A summary of the adsorption properties of these molecules can be found in Table 6.2. For the Z_0 systems, both pyridine and CD₃CN adsorb *ca*. 10 kcal/mol more strongly to the T7 "side" site than to either of the "top" sites. The adsorption geometry of CD₃CN, in Figure 6.5(a)-(c), helps to illustrates the reason for this significant difference. When CD₃CN adsorbs from the "side" pore, the N interacts directly with the framework Zn atom, while in both "top" structures the N atom interacts with one of the protons in the pore. Coordination of the N atom to protons in the "top" sites and Zn from the "side" site is also observed for the pyridine adsorption structures. Considering that 7 of the 9 possible Zn substituent positions in BEA can be found at the intersection of two pores, it is not unexpected to think that framework-substituted Zn would be accessible to incoming adsorbates. The preferential adsorption of pyridine to the Zn atom over the protons of the silanol groups in the Z₀ site support the experimental observation of no IR peak indicative of pyridium ions and Brønsted acidity in these materials.

Table 6.2. Adsorption properties for deuterated acetonitrile and pyridine adsorption.

		Zo			\mathbf{Z}_2	
ΔH_{ads} (kcal mol ⁻¹)	Т5 "Тор"	Т7 "Тор"	T7 "Side"	Т5 "Тор"	Т7 "Тор"	T7 "Side"
Pyridine	-26.4	-26.5	-35.3	-26.9	-27.4	-24.0
$CD_{3}CN$	-16.9	-14.1	-24.7	-21.5	-20.2	-20.4
$\delta_{C\equiv N Freq.}^*$ (cm ⁻¹)						
CD_3CN	-31	-24	-5	-49	-43	-39
* Change in frequency taken with respect to the C=N frequency of CD ₃ CN calculated in a vacuum at						
the same theory level						



Figure 6.5. Adsorption geometries of deuterated acetonitrile on (a) T5, "top", Z₀; (b) T7, "top", Z₀; (c) T7, "side", Z₀; (d) T5, "top", Z₂; (e) T7, "top", Z₂; (f) T7, "side", Z₂ active site models. The natural population analysis charges of the N and neighboring C atoms of the deuterated acetonitrile are shown for each structure. Atoms beyond the Si-atoms immediately neighboring the Zn atom have been shown as wireframes for clarity.

Adsorption strengths of CD₃CN and pyridine onto the Z₂ sites are all calculated within 3 kcal/mol, per species. These values can be easily explained, again, through examination of the CD₃CN adsorption geometries (Figures 6.5(d)-(f)). In the Z₂ structures, the N preferentially coordinates to Li⁺ for all active site models – even from the "side" pore (a trend also shown for pyridine adsorption). The larger Li⁺ of the Z₂ active site preferentially coordinate these adsorbates, blocking access to the framework Zn. The reason for the preferential coordination to the Li⁺ becomes clear when we visualize the lowest unoccupied molecular orbitals (LUMO) of the Z₀ and Z₂ structures, shown in Figure 6.6. Adsorption of pyridine and CD₃CN occurs through the unpaired electrons of the N atoms. In both active site models, the LUMO is localized on the Zn and protrudes into the "side" pore. The relative size of the atoms in Figure 6 is representative of their relative van der Waals radii, and it can be seen that the Li atom size is significantly larger than that of the proton. Its larger size extends further into the "side" pore, blocking access to the LUMO surrounding the Zn atom.

The weaker adsorption of CD₃CN correlates with a weaker polarization of the C=N bond. Adsorption to a proton or the Li⁺ in the Z₀ and Z₂ structures results in a difference in C and N charges of *ca*. 0.9, while adsorption to the Zn atom from the "side" pore of the Z₀ active site has a larger charge difference of *ca*. 1.1. The resulting vibrational frequency of the CD₃CN shows a redshift of *ca*. 40 cm⁻¹ in the Z₂ structures when coordinated to a Li⁺, *ca*. 25 cm⁻¹ in the Z₀ structures when coordinated to H⁺, and only 5 cm⁻¹ in the Z₀ structure when coordinated to Zn. The redshifting of the CD₃CN peak of *ca*. 15-35 cm⁻¹ when coordinated to a Li⁺ are consistent with the relative shift in the experimentally observed peaks at 2290 cm⁻¹ and 2311 cm⁻¹, attributed to two distinct Lewis acid sites [33].



Figure 6.6. Lowest unoccupied molecular orbital (LUMO) visualizations for the (a) Z_0 and (b) Z_2 structures with Zn substituted in the T7 position with the "side" pore modeled.

6.3.3 Furan aromatization

The aromatization of furans with ethylene is known to proceed via tandem Diels-Alder cycloaddition and dehydration reactions, shown in Figure 6.7 [19, 26, 27, 126-128]. Under reaction conditions, the oxanorbornene intermediate formed from the Diels-Alder cycloaddition is unable to be isolated, and therefore separating the catalytic effects of Diels-Alder cycloaddition and dehydration is not possible. Computational studies of the reactions, however, can be used to study the elementary steps of the full reaction profile. The first step in the dehydration mechanism, C-O cleavage of the bridging oxygen of the oxanorbornene, has been shown to be the highest reaction barrier in uncatalyzed and catalyzed reaction mechanisms, and therefore has been chosen as the focus of the current discussion of catalytic effects [26, 27, 126-128].



Figure 6.7. Aromatization reaction scheme for substituted furans with ethylene.

The catalytic effect of both Brønsted and Lewis acidic zeolites on the Diels-Alder reaction have been shown to be negligible, other than the possible entropic confinement effects within the zeolite pores [27, 126, 127]. The calculated Diels-Alder reaction barriers on both Z_0 and Z_2 active sites are consistent with these results (Figure 6.8). All calculated apparent reaction barriers are within 4 kcal/mol of the uncatalyzed reactions. Frontier molecular orbital (FMO) theory has predicted the potential activity of Lewis acid catalysts on Diels-Alder cycloaddition reactions through the minimization in the energy difference of the frontier orbitals of the diene (furan) and dienophile (ethylene) [26, 27, 160]. The furans in this study are being affected by two components of the system; the oxygenated side groups of MMFC and DMFDC and their preferential adsorption to the acid sites. Both act to withdraw electron density from the furan and lower the energy of its lowest unoccupied molecular orbital (LUMO). Unfortunately, these effects activate the inverse electron demand pathway for the Diels-Alder reaction, which is significantly less effective at catalyzing DA cycloaddition than the normal electron demand case [26, 27].

The C-O cleavage reaction barriers are affected by these catalytic active sites. The bridging oxygen of the MMFC cycloadduct is preferentially cleaved from the carbon bonded to the methoxymethyl substituent, whereas DMFDC contains ester



Figure 6.8. Reaction profiles of the first two elementary steps of the reaction of ethylene with (a) MMFC with Z₀ active sites, (b) DMFDC with Z₀ active sites, (c) MMFC with Z₂ active sites, and (d) DMFDC with Z₂ active sites.

groups on both carbon atoms. For the Z_0 active site, the C-O cleavage barrier of MMFC is lowered to 28-37 kcal/mol when interacting with a proton from the "top" pore (Figure 6.8(a)). The transition state for the C-O bond cleavage involves a proton transfer from a silanol of the active site to the bridging oxygen (Figure 6.9(a) and (b)), consistent with the enforced general acid catalysis mechanism seen in previous studies [126, 127]. An even greater reduction in the C-O cleavage barrier is calculated, however, for Z_0 from the "side" pore. In this system, the bridging O of the oxanorbornene directly interacts

with the framework Zn atom (Figure 6.9(c)), and the reaction barrier is lowered to 21 kcal/mol.

The DMFDC cycloadduct shows significantly higher dehydration barriers for all Z_0 active sites studied (Figure 6.8(b)). All catalyzed reaction barriers are higher than for MMFC (41-50 kcal/mol), even when the DMFDC transition state is coordinated to the framework Zn from the "side" pore (Figure 6.9(d)). Considering the similarity between the transition state structures of MMFC and DMFDC, this significant difference in reaction barrier are attributed to the methoxymethyl and ester substituents, respectively. The ester groups on both sides of DMFDC are able to create a resonance structure through the furan ring (Figure 6.10) and effectively withdrawing electron density from the ring and stabilizing the bridging C-O bonds.

At the Z_2 active sites (Figures 6.8(c) and (d)), reaction barriers are generally higher when compared to the Z_0 sites for both reactants. For all transition states found on the Z_2 sites, the reactant molecules coordinate to pore Li⁺ (Figures 6.9(e)-(h)). Reaction barriers calculated for MMFC are 34-44 kcal/mol – similar to those on the Z_0 "top" sites when the reactant molecule coordinated to protons in the pore. For DMFDC, the reaction barriers are all very high, *ca.* 55-58 kcal/mol, within 5 kcal/mol of the uncatalyzed reaction barrier. The weaker Lewis acid strength towards dehydration reactivity is consistent with barriers calculated for other ion-exchanged Lewis acid systems [26, 27].

These reaction profiles support the experimental observations of Orazov and Davis – that the Z_0 site was more active towards aromatization than the Z_2 site and that MMFC was a more reactive furan than DMFDC [33]. The lowest reaction barrier is calculated for MMFC coordinated to a framework Zn atom. If access to the framework



Figure 6.9. Transition state geometries of the C-O cleavage elementary step for (a) MMFC on T5, "top", Z₀; (b) MMFC on T7, "top", Z₀; (c) MMFC on T7, "side", Z₀; (d) DMFDC on T7, "side", Z₀; (e) MMFC on T5, "top", Z₂; (f) MMFC on T7, "top", Z₂; (g) MMFC on T7, "side", Z₂; and (h) DMFDC on T7, "side", Z₂ active site models. Atoms beyond the Si-atoms immediately neighboring the Zn atom have been hidden for clarity.



Figure 6.10. Resonance structure of DMFDC.

Zn site is blocked, however, either by the protons of the Z_0 site from the "top" pore or Li⁺ of any of the Z_2 sites, the reaction barrier increases by *ca.* 10-20 kcal/mol. The framework, Lewis acidic Zn sites have the highest activity for C-O cleavage – even greater than the Brønsted acidic pathway involving the silanols of the Z_0 site. This enhanced lowering of the reaction barrier by the Zn site seems to be due to its abilities

as a strong Lewis acid and the relative weakness of the silanol groups in these materials as Brønsted acids.

The DMFDC reaction barriers are consistently higher on both active sites. Methyl substituents on the furan molecule have been shown to have a moderate effect on the C-O cleavage barrier (*ca.* 10 kcal/mol) [127, 128]. The electron withdrawing activity of the ether groups of DMFDC cause a similar increase in the C-O cleavage barrier. Often, the concerns related to the use of oxygenated side groups of reactants stems from their increased potential to participate in coking, causing catalyst deactivation. The higher reaction barriers calculated for these reactants demonstrate that the side-groups effect on the dehydration reaction is also an important consideration for aromatic selectivity.

6.4 Conclusions

Active site characterization has been performed on zeolites containing framework-substituted Zn atoms. Two classes of active sites have been studied – a Z_0 active site where the framework charge was balanced by two pore protons and a Z_2 active site where the framework charge was balanced by two Li⁺. NBO and Bader analysis of the active site showed Zn incorporation into the zeolite framework through weak ionic bonding to the neighboring O. Differences in the two active sites were found through adsorption studies, where the strongest adsorption was observed when adsorbates were able to coordinate to framework Zn atoms. This was only possible through a "side" pore model of the Z_0 active site, where Zn access was not blocked from the "top" pore by H⁺ or Li⁺ or from the "side" pore by Li⁺.

These differences in the active sites affected reaction barriers for the aromatization of oxygenated furans over these sites. These materials showed negligible catalytic effects on the Diels-Alder cycloaddition reaction of the oxygenated furans with ethylene. The C-O cleavage barrier for dehydration demonstrated differences based on both the nature of the active site and the substituent groups. Two experimental trends were supported by these calculations; the Z_0 site was a better aromatization catalyst than the Z_2 site and MMFC aromatization was more facile than that of DMFDC.

6.5 Future work

The material in this chapter is representative of our progress to-date on the characterization of these materials and their catalytic activity. Work remains to both fully characterize the existing systems and potentially investigate other aspects of the system.

 Z_1 sites are being added to the characterization study to ensure that differences are not seen in these active sites. In addition, calculations of the full reaction profiles for the three elementary steps of the dehydration reaction are in the process of being completed to ensure a shift in rate-limiting step is not observed in the catalytic reaction profiles. Additional natural population analysis of atomic charges and Bader analysis of the electron density at the bond critical points of reactants are being performed to provide a more fundamental understanding of the role of acid sites and substituents on the reactivity.

Additional studies could be used to further validate the conclusions, herein. Modeling Zn substituted into a T-site in the class of T1-T4 substituent atoms could provide information on whether the accessibility of Zn from an intersecting pore is applicable to other T-site structures, or if it was a unique property of the T7-T9 class of substituents. In addition, decarboxylation of DMFDC as a competitive side reaction was shown to be higher in materials with a greater abundance of Z_2 sites [33]. Investigations into this side-reaction could demonstrate whether this is due to catalysis of this decarboxylation, or rather a decrease in selectivity due to less favorable dehydration towards the desired aromatics.

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Chapter 7

SUMMARY AND OUTLOOK

7.1 Computational Modeling of Zeolite Catalysts

The study of heterogeneous, zeolite catalysts in this dissertation has followed a consistent approach. Experimental studies have been instrumental in identifying new materials to study for the aromatization of furans with ethylene. These advances have led to steady increases in aromatic selectivities and yields [19, 21, 25, 29, 30, 33]. Characterization studies, such as microcalorimetry, temperature programmed desorption (TPD), temperature programmed reactions (TPR), solid-state nuclear magnetic resonance (NMR), and adsorption IR, provide valuable information about the presence and nature of active sites in these zeolitic materials [25, 29, 30, 32, 33, 84-87, 92, 93, 131, 136, 189]. Experimental studies of the chemical reactions provide observations about changes in reaction rate, product selectivity, and catalyst stability [19-21, 25, 29-33, 128]. Additionally, experimental kinetic studies provide details about apparent activation energies and reaction orders [31, 32, 126, 128]. These types of experimental studies were critical to narrowing the scope for computational studies.

There is a tremendous amount of insight to be gained from the computational modeling of these zeolite catalysts. Leveraging tools to investigate properties of the material at different length and time scales can provide a tremendous amount of information on the fundamentals of the materials and reactions that lead to the experimental observations. The importance of these different scales to the problem is evident in Chapter 3, where two kinetic regimes were discovered for the aromatization
of DMF and ethylene with H-Y zeolites. First principles studies conducted on the tandem Diels-Alder cycloaddition and dehydration of DMF and ethylene to p-xylene showed the dehydration barrier to be the rate-limiting step in the uncatalyzed system. The addition of an H-Y catalyst lowered the dehydration barrier, causing a change in the highest energy barrier in the reaction pathway to that of the Diels-Alder cycloaddition. Only when a microkinetic model was built and used to probe the overall reaction kinetics were the experimental observations made at different catalyst loadings explained. At high acid site concentrations, the uncatalyzed Diels-Alder reaction was rate-limiting, as predicted by the DFT calculated reaction profile. At low acid site concentration, however, there was a change in the rate-determining step to that of the catalyzed dehydration reaction (in spite of its lower catalyzed reaction barrier), with a commensurate change in the apparent activation energy and reaction orders. It was found that at low acid site concentration conditions, the concentration of reactants at zeolitic active sites becomes important for the overall rate of p-xylene production; a conclusion which is not evident when examining the reaction profile, alone.

In Chapter 2, a detailed study was carried out to improve the accuracy of calculated adsorption enthalpies in zeolites. As is always the case with first principles DFT calculations, limits in computational resources lead to a tradeoff between accuracy and speed. A model of a complete zeolite particle would be impossible, owing to its tremendous size. The size of the system, therefore, is decreased by "cutting out" region around the local active site from the larger zeolite pore. The smallest such models, which only consider the acid site and framework atoms in its immediate vicinity, can be very accurate for the calculation of reaction barriers, but fail to accurately calculate adsorption strengths where the dispersive forces from the extended zeolite pore become

important. By treating the local active site with high quality DFT calculations and the extended zeolite pore with less-expensive molecular mechanics methods, the accuracy of the model was significantly improved without the affecting the computational time. This type of approach is pivotal if these systems are to be leveraged for detailed reaction profile calculations.

The potential impact of errors in the DFT calculated values became evident in Chapter 5, where considerable discussion was given to the effect of the calculated homogeneous Diels-Alder cycloaddition barrier. At high acid site concentrations, this rate is shown to be rate-determining for *p*-xylene production. Small errors in the DFT calculated values were shown to have significant effects on the predicted plateau in the rate of *p*-xylene production. When calculated at one DFT level of theory, the plateau in the reaction rate was an order of magnitude slower than measured experimentally, while use of a more accurate theory level showed a decrease the reaction barrier of *ca.* 3 kcal/mol, resulting in a rate twice that of the experimentally measured value. This difference of 3 kcal/mol in the calculated reaction barrier, representing an error of less than 10% of the calculated value, is shown to affect the rate by an order of magnitude. Simple kinetic analysis of the system run at 250 °C makes this conclusion evident, but does not change the fact that it is an important consideration for modeling accuracy. In this particular study, the two different theory levels did not affect the qualitative conclusions of the study, enabling relevant discussions of the overall system. The homogeneous Diels-Alder reaction barrier was identified as a critical value to accurately predict reaction rates with potential errors which could be important to consider for studies in different solvents.

Errors in computed parameters are not the only ways in which model inaccuracies arise. At the reactor scale, a failure to account for all relevant reaction steps in a kinetic reactor model can be equally impactful. This was seen in Chapter 4, for the aromatization of furan to benzene. The aromatization of furan and 2,5-dimethylfuran to benzene and *p*-xylene, respectively, have the same reaction mechanisms and, therefore, the same elementary steps were used in the construction of the microkinetic model. DMF selectivities to *p*-xylene and 2,5-hexanedione demonstrated very good agreement over both H-[B]-BEA and H-[Al]-BEA. The reaction involving furan substantially overpredicted the selectivity to benzene over both zeolite catalysts. Significant catalyst coking observed experimentally when starting with a furan reactant help explain the inherent error in the model. Oligomerization reactions not accounted for in the model must be contributing to the selectivity loss. Without methyl protecting groups of DMF at the α -C positions for furan, significant side reactions appear to play a major role. These oligomerization reactions are difficult to characterize experimentally, without useful analytical tools for assessing the coking side-products left behind in the zeolite pores, and therefore make targets for computational studies difficult. Nonetheless, this error identifies these oligomerization reactions as a primary target for improved selectivity of these reactions, especially when considering different furan substituents.

7.2 The Role of Brønsted and Lewis Acidity

Major advancements from this thesis include significant progress in the understanding of the role of the active sites in these solid acid zeolitic materials. As discussed in Chapter 2, the improvement started by developing an improved model of the zeolite catalysts by accounting for both the active site and the surrounding pore. This improvement gave us confidence to begin investigating systems beyond the wellunderstood, Al substituted Brønsted acidic zeolites.

In Chapter 4 a study investigated the effects of Brønsted acid strength on reactivity. This was done by fundamentally changing the substituent atom from Al to another metal, such as B, Ga, and Fe. Measurements of the Brønsted acid strength, such as adsorption strength, IR spectra, or calculated deprotonation energies provide a quantitative measure of acid strength in these solid acid catalysts. It is important to note, however, that when examined from the vantage of elementary reaction steps, principles of enforced general acid catalysis demonstrated when these measures of acid strength could be expected to translate into differences in chemical reactivity. In elementary steps involving a proton transfer from the zeolite (e.g. C-O bond cleavage), a strong correlation could be drawn between measures of acid strength and reactivity, while in those steps where no proton transfer was involved (e.g. nucleophilic attack of the protonated furan by water) no correlation was observed. These types of effects must be considered when thinking about the effect of different catalysts for reactivity. Through understanding the nature and role of these Brønsted acid sites on activity, H-[B]-BEA was accurately predicted to be an active catalyst for furan aromatization, as confirmed experimentally. From this, it is clear that understanding the role of not only the catalyst, but also the reactions themselves is important to designing experiments to compare acid strength in new materials moving forward.

The framework-substituted Lewis acid zeolites in Chapters 5 and 6, provided two complicating factors. These were systems where fundamentally less was known about the nature of the active sites and Diels-Alder and dehydration reaction effects could not be separated experimentally. In the case of Sn-, Ti-, and Zr-BEA in Chapter 5, experimental and computational studies showed possible Lewis acidic "closed" sites and "open" sites were complicated by the presence of Lewis acid centers adjacent to Brønsted acidic silanols. Similarly, in Chapter 6, the Lewis acid nature of the active site was complicated by the types of pore cations and, in the case of Z_0 , the presence of Brønsted acidic silanols. DFT calculations were able to eliminate the possibility of DA catalysis in these systems, in spite of their Lewis acid character. Instead, for the first time Lewis acid sites strong enough to catalyze cycloadduct dehydration were discovered. These results remain complicated by the fact that the Brønsted acidic silanols also catalyze the reaction by the same enforced general acid catalysis mechanism shown for the purely Brønsted acidic zeolites.

In spite of these complications, these findings point in a promising direction moving forward. First, and most importantly, Lewis acids were discovered capable of catalyzing the aromatization of furans. This opens up tremendous potential when thinking about possible materials to run these reactions with improved selectivity if not limited to Brønsted acid sites to catalyze the dehydration reaction. Second, even though there are Brønsted acidic silanol groups in these materials, they appear to be measurably weaker than standard Brønsted acidic zeolites, as evidenced computationally and the continual improvement in product selectivity. Even oxygenated furans, highly susceptible to coking side reactions, are able to be converted with these materials. The potential remains for a purely Lewis acidic material capable of achieving even higher selectivities from an even wider array of starting reactants.

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Appendix A

ADSORPTION IN ZEOLITES USING MECHANICALLY EMBEDDED ONIOM CLUSTERS – SUPPORTING INFORMATION

A.1. quasi-Rigid Rotor Harmonic Oscillator approximation (qRRHO)

It is well known that treating the translational or rotational degrees of freedom of a guest molecule in a host molecule (*e.g.*, zeolite) as low-frequency harmonic oscillations results in inaccurate thermal corrections. In the limit of zero frequency, the vibrational energy of the harmonic oscillator approaches kT instead of kT/2, which is the correct contribution of a translational or rotational degree of freedom. In the same limit, the entropy of a harmonic oscillator diverges to infinity.

Following Head-Gordon [71], we use Equations A.1-A.3 to compute the vibrational thermal energy and replace frequencies below a cut-off frequency of 100 cm⁻¹ with kT/2 by means of a switching function : $\omega(v_i)$

$$U_{qRRHO} = \sum_{i} \left[\omega(\nu_i) U_{RRHO} + \left(1 - \omega(\nu_i) \right) \frac{1}{2} RT \right]$$
(A.1)

$$U_{HO} = \frac{1}{2} N_A h v_i + RT \left(\frac{h v_i}{kT}\right) \frac{e^{-h v_i/kT}}{(1 - e^{-h v_i/kT})}$$
(A.2)

$$\omega(\nu_i) = \frac{1}{1 + (\nu_0/\nu_i)^4} \tag{A.3}$$

where v_i is the vibrational frequency, v_0 is the cut-off frequency (chosen to be 100 cm⁻¹), N_A is Avogadro's number, *h* is Planck's constant, *k* is Boltzmann's constant, and *T* is temperature.

In the qRRHO approximation to the entropy proposed by Grimme [89], the lowfrequency contributions to the vibrational entropy of the harmonic oscillator are replaced by a corresponding rotational entropy:

$$S_{qRRHO} = \sum_{i} \left[\omega(\nu_i) S_{HO} + \left(1 - \omega(\nu_i) \right) S_{RR} \right]$$
(A.4)

$$S_{RR} = R \left[\frac{1}{2} + \ln \left\{ \left(\frac{8\pi^3 \mu' kT}{h^2} \right)^{1/2} \right\} \right]$$
(A.5)

$$\mu' = \frac{(h/8\pi^2 v_i)B_{av}}{(h/8\pi^2 v_i) + B_{av}}$$
(A.6)

$$S_{HO} = R \left[\frac{h\nu_i}{k(e^{h\nu_i/kT} - 1)} - \ln(1 - e^{-h\nu_i/kT}) \right]$$
(A.7)

where B_{av} is an average molecular moment of inertia chosen to be 10⁻⁴⁴ kg m².

A.2. Calculated entropies of adsorption

In Table S1, we present the calculated entropies of adsorption within the qRRHO approximation for adsorption of n-C₁ to n-C₈ alkanes in H-MFI and compare with experimental values reported by De Moor *et al.*[97] For the guest molecule, we have assumed 2-dimensional free translations on a molecular surface area of 200 pm × 600 pm [97].

Temperature (°C)	Exp.	25	50	75	100	125	150	200
Methane		-59.3	-58.1	-57.0	-56.0	-55.1	-54.2	-53.3
Ethane		-76.7	-76.0	-75.3	-74.7	-74.1	-73.5	-72.9
Propane	-94	-101.9	-101.4	-101.0	-100.5	-100.1	-99.7	-99.3
<i>n</i> -Butane	-104	-112.5	-112.0	-111.6	-111.2	-110.9	-110.5	-110.1
<i>n</i> -Pentane	-118	-120.5	-120.1	-119.8	-119.5	-119.2	-118.9	-118.6
<i>n</i> -Hexane	-121	-126.2	-125.9	-125.7	-125.4	-125.2	-125.0	-124.7
<i>n</i> -Heptane		-148.8	-148.8	-148.8	-148.8	-148.8	-148.7	-148.7
<i>n</i> -Octane		-159.4	-159.7	-160.0	-160.2	-160.4	-160.6	-160.8

Table A.1. Adsorption entropies within the qRRHO approximation.

Appendix B

KINETIC REGIME CHANGE IN THE TANDEM DEHYDRATIVE AROMATIZATION OF FURAN DIELS-ALDER PRODUCTS – SUPPORTING INFORMATION

B.1. Investigation of gas-to-liquid mass transfer limitations



Figure B.1. A) Kinetic data used to determine k_{rxn} . B) Pressure drop upon start of the gas dispersion impeller to acquire the mass transfer coefficient k_{la} .

To ensure that the experiments were not mass transfer limited, the second Damköhler number was determined. A series of kinetic data was measured in the cycloaddition limited reaction at 250 °C and 1.38 M DMF to obtain the rate constant for the maximum observed rate. Mass transfer tests were performed by adding the standard volume of heptane to the reaction vessel (60 ml for the small reactors and 100 ml for

the large reactor) and pressurizing to *ca*. 800 psi with ethylene. Once the reactor was pressurized, the gas dispersion impeller was turned to 1000 rpm and the system pressure was monitored with $1/24^{\text{th}}$ of a second accuracy. Temporal pressure changes were extracted from this video which can be directly correlated to an effective increase in solution phase ethylene to obtain a k_la value. The second Damköhler number is the ratio of the k_{rxn}/k_la and gives a value well below the value of 0.1, indicative of no mass transfer limitation. Both of the concentrations for DMF and ethylene were scaled to one for easier visual comparison of the slopes.





Figure B.2. Abridged network of all reactions considered in this work.

Table B.1. Energetics of all reactions considered in the microkinetic model.

 Adjustments made to QM/MM calculated entropy values are shown in parentheses.

Reaction ^b	$\Delta H^{\ddagger_{i,250^\circ C}b,d}$	$-\Delta S^{\ddagger_{i,250^{\circ}C}c,d}$	ΔH^{\ddagger} -i,250°C ^{b,d}	- ΔS^{\ddagger} -i,250°C ^{c,d}				
$DMF + E \rightleftharpoons CA$	23.1	31.2 (-2.4)	33.0	-17.6 (-12.9)				
$DMF * + E \rightleftharpoons CA$	25.3	34.6	51.5	-16.7				
$CA \rightarrow Int1$	61.6	-2.8	58.1	0.9				
$Int1 \rightarrow Int2$	48.2	0.3	52.8	3.0				
$Int2 \rightarrow pX + W$	47.9	0.1	71.2	34.6				
$CA * \rightarrow Int1 *$	14.5	-0.2	8.2	7.6				
$Int1 * \rightarrow Int2 *$	8.7	6.4	29.3	-1.9				
$Int2 * \rightarrow pX + W *$	14.3	-6.7	23.2	38.0				
$DMF * + W \rightleftharpoons HDI *$	21.1	-5.5	35.1	-26.4				
Adsorption/Desorption ^b	Ki	$\Delta G_{ads,250^\circ C}{}^d$						
$CA + * \rightleftharpoons CA *$	-25.8	45.9 (+10.1)						
$W + * \rightleftharpoons W *$	-11.1	26.2						
$DMF + * \rightleftharpoons DMF *$	-17.9	27.1 (-5.7)						
$HDI + * \rightleftharpoons HDI *$	-25.9	36.3						
$E + * \rightleftharpoons E *$	-9.0	23.0						
$pX + * \rightleftharpoons pX *$	-16.6	35.3						
$Hept + * \rightleftharpoons Hept *$	-11.4	33.4						
^a Molecules are labeled as follows: 2,5-Dimethylfuran (DMF), Ethylene (E), Cycloadduct (CA), p-Xylene (pX),								
Water (W), 2,5-Hexanedione (HDI), Heptane (Hept), Vacant Acid Site (*); ^b Enthalpies are tabulated in units of								
kcal mol ⁻¹ ; ^c Entropies are tabulated in units of cal mol ⁻¹ K^{-1} ; ^d Subscript "i" implies forward reaction while "-								

B.3. Development of rate expressions

B.3.1. Unimolecular reaction in liquid phase or on surface

Assume an irreversible reaction of the type

$$A \xrightarrow{k} B$$

i" implies reverse reaction.

According to transition state theory (TST), the reaction proceeds through a short-lived activated complex, $A^{\!\scriptscriptstyle +\!\!\!-}$.

$$A \xleftarrow{k_1 \& k_{-1}} A^{\pm} \xrightarrow{k'} B$$

The concentration of B therefore depends on the conversion rate of the activated complex to the product.

$$\frac{d[B]}{dt} = k \cdot [A] = k' \cdot [A]^{\pm}$$

At the same time, reactant and activated complex are in thermodynamic quasiequilibrium

$$K_{eq}^{\pm} = rac{[A]^{\pm}/[A]^{\pm^0}}{[A]/[A]^0}$$

Index 0 indicates the *standard state*. We define the standard state of compounds in solution as $S^{0}_{hom} = 1 \text{ mol/}L_{liquid}$. The standard state for the reactant equals that of the transition state, and hence cancels in the above expression. Solving this equilibrium expression for the concentration of the activated complex gives

$$\frac{d[B]}{dt} = k' \cdot [A]^{\pm} = k' \cdot K_{eq}^{\pm} \cdot [A]$$

where κ is the transmission coefficient (assumed to be unity) in

$$k' \cdot = \kappa \cdot \frac{k_B \cdot T}{h}$$

and

$$K_{eq}^{\pm} = \exp\left\{\frac{-\Delta G^{\pm}}{R \cdot T}\right\} = \exp\left\{\frac{\Delta S^{\pm}}{R}\right\} \cdot \exp\left\{\frac{-\Delta H^{\pm}}{R \cdot T}\right\}$$

Thus,

$$k = k' \cdot K_{eq}^{\pm}$$

and

$$\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -k_1 \cdot [A].$$

B.3.2. Rate expression of bimolecular reactions

First we consider the forward reaction

$$A + B^* \xrightarrow{k_{forward}} C^*$$

According to TST, the reaction proceeds through a short-lived activated complex. $A + B^* \xleftarrow{k_1 \& k_{-1}} (AB^*)^{\pm} \xrightarrow{k'} C^*$

The concentration of C^* therefore depends on the conversion rate of the activated complex to the product

$$\frac{d[C^*]}{dt} = k_{forward} \cdot [A] \cdot [B^*] = k' \cdot [AB^*]^{\pm}$$

The reactants are in thermodynamic quasi-equilibrium with the activated complex

$$K_{eq}^{\pm} = \frac{k_1}{k_{-1}} = \frac{[AB^*]^{\pm} / [AB^*]^{\pm 0}}{[A] \cdot [B^*] / [A]^0 \cdot [B^*]^0}$$

Index *0* indicates the *standard state*. The standard state of all adsorbed and solutionphase species is defined as $S^{0}_{ads} = 1$ site/cm³_{zeolite} and $S^{0}_{hom} = 1$ mol/L, respectively. The transition state, $[AB^*]^{+-}$, occurs after solution-phase species A has approached adsorbed B* and thus its standard state is that of an adsorbed species. After solving the equilibrium expression for the concentration of the activated complex, we obtain

$$\frac{d[C^*]}{dt} = k' [AB^*]^{\pm} = k' \cdot K_{eq}^{\pm} \cdot \frac{[A] \cdot [B^*]}{[S_{hom}^0]} = k_{forward} \cdot \frac{[A] \cdot [B^*]}{[S_{hom}^0]}$$

Next, we consider the backward reaction

$$C^* \xrightarrow{k} A + B^*$$

According to TST, the reaction proceeds through a short-lived activated complex $C^* \xleftarrow{k_1 \& k_{-1}} (AB^*)^{\pm} \xrightarrow{k'} A + B^*$

The concentration of both A and B^* therefore depends on the conversion rate of the activated complex to the product

$$\frac{d[A]}{dt} = \frac{d[B^*]}{dt} = k \cdot [C^*] = k' [AB^*]^{\pm}$$

The reactant is in thermodynamic quasi-equilibrium with the activated complex

$$K_{eq}^{\pm} = \frac{k_1}{k_{-1}} = \frac{[AB^*]^{\pm}/[AB^*]^{\pm 0}}{[C^*]/[C^*]^0}$$

After solving the equilibrium expression for the concentration of the activated complex, we obtain

$$rate_{backward} = k' \cdot [AB^*]^{\pm} = k' \cdot K_{eq}^{\pm} \cdot [C^*] = k_{backward} \cdot [C^*]$$

B.2.3. Adsorption and desorption

For all reactants, products and stable intermediates of the reaction network, the rates for adsorption and desorption were found to be several orders of magnitude faster than for reactive steps and thus all adsorbed species were assumed to be at equilibrium

with the solution phase species at all times. We can easily derive the adsorption equilibrium if we replace B* and C* with vacant site * and adsorbed species A, A*, in the equation above

$$A + * \xleftarrow{}^{k_{fadsorption} & \&k_{desorption}} A *$$

$$rate = rate_{adsorption} - rate_{desorption} = 0$$

$$\Leftrightarrow k_{adsorption} \cdot \frac{[A] \cdot [*]}{[S_{hom}^{0}]} = k_{desorption} \cdot [A^*]$$

$$\Leftrightarrow C_{A^*} = K_{adsorption} \cdot \frac{[A][*]}{[S_{hom}^{0}]}$$

where $K_{adsorption}$ is the adsorption equilibrium constant which we calculate using the free energy of adsorption, $\Delta G_{adsorption}$, as

$$K_{adsorption} = \exp\left\{\frac{-\Delta G_{adsorption}}{R \cdot T}\right\}$$

The equilibrium expressions are solved along with the site balance considering all adsorbed species

$$[H+]^{Z_{t}} = [H+]^{Z} + \sum_{i=1}^{n} [i^{*}]$$

B.2.4. Rate constant models

Relevant rate constant models and explanations can be found in standard statistical mechanics literature [40, 190]. For adsorbed species, only the vibrational partition function was considered. Using standard nomenclature and labeling, the following equations were used

$$k_{reaction} = \frac{Q^{\pm}}{Q_{reac \tan t}} \cdot \frac{k_B \cdot T}{h} \cdot \exp\left(-\frac{\Delta E^{\pm}}{k_B \cdot T}\right)$$
$$Q_{liquid_phase} = q_{trans} \cdot q_{rot} \cdot q_{vib}$$
$$Q_{adsorbed} = q_{vib}$$

$$q_{trans} = \left(\frac{2 \cdot \pi \cdot m \cdot k_B \cdot T}{h^2}\right)^{3/2} \cdot \frac{k_B \cdot T}{P}$$

$$q_{vib} = \prod_i \frac{\exp\left(-\frac{h \cdot v_i}{2 \cdot k_B \cdot T}\right)}{1 - \exp\left(-\frac{h \cdot v_i}{k_B \cdot T}\right)}$$

$$q_{rot} = \frac{\left(\pi \cdot I_A \cdot I_B \cdot I_C\right)^{1/2}}{\sigma} \cdot \left(\frac{8 \cdot \pi^2 \cdot k_B \cdot T}{h^2}\right)^{3/2}$$

B.4. Design of experiment (DOE) to access model uncertainty

First, a minor adjustment of 1.25 kcal/mol in the Diels-Alder reaction energy resulted in the *p*-xylene production rate matching the expected experimental rate of *ca*. 9 mmol/hr. Second, a DOE methodology was employed to access combinations of parameters of the MKM that provide responses consistent with a set of four experimental measurements, namely the rate of *p*-xylene production, the reaction orders with respect to DMF and ethylene, and the apparent activation energy at both 1.3 mM and 5.1 mM of catalyst loading. Five model parameters were tested: the endothermicity of the homogeneous DA reaction, the reaction barrier of the first step of the heterogeneous dehydration reaction, and the strength of adsorption of DMF, 2,5hexanedione, and the oxanorbornene intermediate. A 3⁵ factorial design was used, where these 5 parameters were changed by 0.0, 2.5, and 5.0 kcal/mol from their firstprinciples calculated values, for a total of 486 runs of the MKM at the two catalyst loadings. The aforementioned parameters were chosen and adjusted guided from initial MKM simulations so that the homogeneous DA reaction was made more endothermic, the heterogeneous dehydration reaction barrier was made larger, the adsorption of DMF was strengthened and those of oxanorbornene and 2,5-hexanedione were weakened.

With this set of data, an ANOVA analysis was performed to investigate the effect of the primary and interaction of the factors on these four responses. For factors considered significant based on their p-value, a linear regression was developed for the response of the calculated experimental parameters to the relevant factors and interaction terms. With a set of eight equations for the four measured experimental values at the two different catalyst loadings, the effect of changing these factors from 0.0-5.2 kcal/mol in 0.4 kcal/mol increments was investigated, for a total of 1,075,648 possible combinations of parameters at the two catalyst loadings. With this entire range of combinations predicted by the set of linear equations, regions where the calculated experimental values were within 12% of the experimentally measured values were searched for. At no point were all four experimental values satisfied for a given catalyst loading, but regions, where three out of the four experimental responses were satisfied, were found. The corresponding regions include a 4.5-5.0 kcal/mol more endothermic Diels-Alder reaction, a 0.0-3.0 kcal/mol higher reaction barrier of dehydration, 2.0-5.0 kcal/mol stronger DMF adsorption, 4.5-5.0 kcal/mol weaker oxanorbornene adsorption, and 0.0-5.0 kcal/mol weaker 2,5-hexanedione adsorption. With a narrowed region of interest, the full MKM was rerun and a final set of parameters was chosen which best represented the experimental measurements. As these adjustments applied to the Gibbs free energies of reaction, adjustments to the given parameters were made to the calculated entropies of the reaction, as shown in Table S1.

In summary, the above methodology is a systematic way to constrain the multiparameter space of the model to reproduce a multi-response surface of experimental data within a certain range as one or more experimental conditions (e.g., the acid cite concentration) vary.

B.5. Reduced model development

Species Rates and Site Balance (Full Model) $r_{DMF} = -k_1[DMF][E] + k_{-1}[CA] - k_6[DMF][*] + k_{-6}[DMF *]$ $r_{DMF*} = -k_3[DMF *][W] + k_{-3}[HDI *] + k_6[DMF][*] - k_{-6}[DMF *]$ $r_E = -k_1[DMF][E] + k_{-1}[CA]$ $r_{CA} = k_1[DMF][E] - k_{-1}[CA] - k_4[CA][*] + k_{-4}[CA *]$ $r_{CA*} = -k_2[CA *] + k_4[CA][*] - k_{-4}[CA *]$ $r_{pX} = k_2[CA *]$ $r_{W} = -k_3[DMF *][W] + k_{-3}[HDI *] - k_5[W][*] + k_{-5}[W *]$ $r_{W*} = k_2[CA *] + k_5[W][*] - k_{-5}[W *]$ $r_{HDI} = -k_7[HDI][*] + k_{-7}[HDI *]$ $r_{HDI*} = k_3[DMF *][W] - k_{-3}[HDI *] + k_7[HDI][*] - k_{-7}[HDI *]$ [H+] = [*] + [CA *] + [W *] + [DMF *] + [HDI *]where [H+] is the total active sites.

Given the low concentrations of cycloadduct in solution and on the catalyst

(species in quasi steady-state), one gets

$$C_{CA} = \frac{(k_{-4} + k_2)}{k_4} \left(\frac{[CA *]}{[*]}\right)$$
$$C_{CA*} = \frac{k_1 k_4 [DMF][E][*]}{(k_{-1}k_{-4} + k_{-1}k_2) + k_2 k_4[*]}$$

The rate of p-xylene is

$$r_{pX} = \frac{k_2 K_1 K_4 [DMF][E][*]}{\left(1 + \frac{k_2}{k_{-4}}\right) + \frac{k_2}{k_{-1}} K_4[*]}$$

Cycloadduct on the surface is in quasi steady-state and the remaining adsorption

and desorption steps are rapidly equilibrated, leading to

$$C_{CA*} = \left(\frac{\kappa_4}{k_{-4} + k_2}\right) [CA][*]$$

$$C_{W*} = K_5[W][*]$$

$$C_{DMF*} = K_6[DMF][*]$$

$$C_{HDI*} = K_7[HDI][*]$$

Substituting into the active site balance equation and rearranging gives [H+]

$$[*] = \frac{[H+]}{\left(\frac{k_4}{k_{-4}+k_2}\right)[CA] + K_5[W] + K_6[DMF] + K_7[HDI]}$$

Comparing the order of magnitude of terms in the denominator (with order of terms in the same order as above)

$$[*] = \frac{[H+]}{O(10^{-8}) + O(10^{-3}) + O(10^{1}) + O(10^{1})}$$

we see that the cycloadduct and the water terms are much smaller than DMF and 2,5hexanedione terms. This makes sense, as seen in Figure 8A, where coverages are high and DMF and 2,5-hexanedione dominate the surface of the zeolite. Therefore, the vacant site balance reduces to

$$[*] = \frac{[H+]}{K_6[DMF] + K_7[HDI]}$$

The rate of *p*-xylene production can thus be computed as

$$\boldsymbol{r}_{\boldsymbol{p}\boldsymbol{X}} = \frac{\left(\frac{k_2 K_1 K_4}{K_6 [DMF] + K_7 [HDI]}\right) [DMF] [E] [H+]}{\left(1 + \frac{k_2}{k_{-4}}\right) + \left(\frac{k_2}{k_{-1}}\right) \left(\frac{K_4}{K_6 [DMF] + K_7 [HDI]}\right) [H+]}$$

The term k_2/k_{-4} indicates the relative rates of heterogeneous dehydration reaction, k_2 , and the desorption of the cycloadduct from the surface, k_{-4} . $k_2/k_{-4} \ll 1$ over a range of relevant temperatures (see figure below) and the rate equation reduces to

$$r_{pX} = \frac{\left(\frac{k_2 K_1 K_4}{K_6 [DMF] + K_7 [HDI]}\right) [DMF] [E] [H+]}{1 + \left(\frac{k_2}{k_{-1}}\right) \left(\frac{K_4}{K_6 [DMF] + K_7 [HDI]}\right) [H+]}$$


Figure B.3. k_2/k_{-4} as a function of temperature over relevant reaction temperature range.

The hydrolysis of DMF with water to 2,5-hexanedione is, also, equilibrated. The concentration of 2,5-hexanedione in solution can be solved for in terms of DMF and water as

$$[HDI] = \left(\frac{K_3 K_6}{K_7}\right) [DMF][W]$$

So that the rate of *p*-xylene production is written as

$$r_{pX} = \frac{\left(\frac{K_2 K_1 K_4}{1 + K_3 C_W}\right) [DMF][E][H+]}{K_6 [DMF] + \left(\frac{k_2}{k_{-1}}\right) \left(\frac{K_4}{1 + K_3 [W]}\right) [H+]}$$

We notice the presence of a water product in our solution. Water is inseparable from the rate of p-xylene production, as they are both produced in the dehydration reaction. Due to the presence of the competitive hydrolysis side-reaction and the competition for active sites by its by-product 2,5-hexanedione, we see that water that is produced acts as a rate inhibitor for this reaction.

Comparing the two terms in the denominator of the full reduced model



Figure B.4. The left hand side of the denominator, $K_6[DMF]$, shown as the blue dotted line versus the right hand side of the denominator, $\left(\frac{k_2}{k_{-1}}\right)\left(\frac{K_4}{1+K_3C_W}\right)[H+]$, shown as a red solid line as a function of solid acid site concentrations.

At sufficiently low acid site concentrations, the right hand side of the denominator becomes very small as compared to the left hand side of the denominator, and the rate of p-xylene production reduces to

$$\left(\frac{k_2K_1K_4}{K_6(1+K_3[W])}\right)[E][H+]$$

We can see the linear dependence on the total acid site concentration. The zero-order kinetics of DMF and first-order kinetics of ethylene are also captured.

On the other hand, as C_{*t} grows larger than *ca*. 5 mM, the right hand side of the denominator can be greater than 1 and the rate of *p*-xylene production reduces to. $r_{pX} = k_1 [DMF][E]$

The rate is independent of the total acid site concentration and exhibits first-order kinetics with respect to DMF and ethylene as expected in the Diels-Alder regime.

B.6. Catalyst preparation and characterization

H-Y faujasite catalyst with a Si/Al ratio of 2.6 (Zeolyst CBV 600) was used for all of the reactions and dried in a furnace at 200 °C prior to use. The number of Brønsted acid sites was characterized by temperature programmed desorption coupled with thermal gravimetric analysis (TPD-TGA) on a thermal analyzer (SDT Q600, TA) for isopropylamine (IPA). The TGA plots indicate a two-step weight change for the samples. According to the literature [189], weight loss at low temperature (<300 ° C) is attributed to desorption of the IPA adsorbed on the weak acid sites, whereas the one between 300 °C and 400 °C is from the decomposition of IPA on strong Brønsted acid sites.

Appendix C

GENERAL ACID-TYPE CATALYSIS IN THE DEHYDRATIVE AROMATIZATION OF FURANS TO AROMATICS IN H-[AL]-BEA, H-[FE]-BEA, H-[GA]-BEA, AND H-[B]-BEA ZEOLITES – SUPPORTING INFORMATION



Figure C.1. ONIOM representation of BEA zeolite. Ball-and-stick representations represent the small layer, tubeframe the intermediate layer, and wireframe the real layer of the ONIOM system. This model shows Al-substituted BEA, where the pink atom is Al, red atoms are O, gray are Si, and white are H.



Figure C.2. Local geometries with bond lengths and angles of (a) H-[Al]-BEA, (b) H-[Ga]-BEA, (c) H-[Fe]-BEA, and (d) H-[B]-BEA. The surrounding ONIOM structure has been removed for clarity and the O-atoms surrounding the framework-substituted metal atom have been numbered for referencing purposes.



Figure C.3. Adsorption strength as a function of DPE.





Figure C.4. Reaction profiles for the dehydration of (a) furan, (b) non-alkyl side of MF, (c) alkyl side of MF, and (d) DMF oxanorbornene intermediates over H-[B,Fe,Ga,A1]-BEA zeolite systems.



Figure C.5. Color change from addition of DMF to (a) H-[Al]-BEA and (b) H-[B]-BEA.



Reaction Coordinate



Figure C.6. Reaction profiles for the hydrolysis of (a) furan, (b) non-alkyl side of MF, (c) alkyl side of MF, and (d) DMF with 1 water molecule in the pore over H-[B,Fe,Ga,Al]-BEA zeolite systems.



Figure C.7. Reaction profiles for the rate-limiting step of hydrolysis of (a) furan, (b) non-alkyl side of MF, (c) alkyl side of MF, and (d) DMF with 2 water molecule in the pore over H-[B,Fe,Ga,Al]-BEA zeolite systems.



Figure C.8. XRD Patterns of H-[Al]-Beta and H-[B]-Beta.



Figure C.9. SEM image of H-[B]-Beta. SEM images were taken with a JSM-7400F scanning electron microscope with an accelerating voltage of 3.00 kV and a current of $10 \mu A$.

<i>T</i> -Atom Charge (q_T)	1.42	2.19	2.01	2.10					
O -Atom Charge (q_0)	- 1.11	- 1.17	- 1.13	- 1.14					
H-Atom Charge (q_H)	0.52	0.55	0.55	0.56					
O-H Ionicity $ q_O q_H $	0.58	0.64	0.62	0.63					
sp Character of T-Atom	sp ^{2.01}		sp ^{2.60}	sp ^{2.49}					
Exper. O-H Frequency $v_{O-H,Exper.}$ (cm ⁻¹)	3740	3630	3620	3610					
Comp. O-H Frequency ^a $v_{O-H,Comp.}$ (cm ⁻¹)	3810	3602	3614	3615					
^a Calculated O-H vibrational frequencies have been scaled by 0.982, the									
Calculated 0-11 vibrational frequencies have been so	caled by	0.982,	the						

Table C.1. Intrinsic properties of the isomorphously substituted H-BEA zeolite models.

vibrational frequency scaling factor recommended for the M06 theory used for the calculations

Table C.2. Reaction profile energies for the Diels-Alder cycloaddition and dehydration of furan, MF, and DMF on B, Ga, Fe, and Al-substituted BEA zeolites.

		DMF Adsorption	DMF + E Adsorption	Diels-Alder Cycloaddition	C-0	Dehydration 1 st Proton	2 nd Proton		
		Ausorption	Ausorption	Cycloaddition	Cleavage	Transfer	Transfer		
	Catalyst	ΔG_{ads} (kcal/mol)	$\begin{array}{c} \Delta G_{ads} \\ (kcal/mol) \end{array}$	$\Delta \mathbf{G}^{\ddagger}_{\mathbf{forw}}$ // $\Delta \mathbf{G}^{\ddagger}_{\mathbf{rev}}$ (kcal/mol)	Z	$\Delta G^{\ddagger}_{forw} // \Delta G^{\ddagger}_{rev}$ (kcal/mol)	7	$\Delta \mathbf{G}^{\ddagger}_{\mathbf{app.,DA}}$ (kcal/mol)	$\Delta \mathbf{G}^{\ddagger}_{app.,Dehy.}$ (kcal/mol)
	Uncatalyzed		6.6	34.1 // 30.0	57.7 // 58.2	50.0 // 58.2	45.7 // 79.1	40.7	68.4
ut	H-[B]-BEA	-2.7	4.3	29.4 // 35.0	30.2 // 12.3	12.6 // 36.9	6.6 // 39.5	33.7	29.2
Fure	H-[Ga]- BEA	-5.0	2.0	29.4 // 41.6	25.1 // 12.1	10.2 // 33.4	7.4 // 37.7	31.3	14.9
	H-[Al]-BEA	-4.6	1.2	29.8 // 41.6	24.6 // 13.1	10.7 // 34.4	11.3 // 39.1	31.0	14.1
ľ	Uncatalyzed		7.2	34.2 // 30.6	52.5 // 51.3	47.1 // 54.9	47.2 // 80.8	41.5	63.4
MF Non-Methy	H-[B]-BEA	-5.4	5.2	29.5 // 35.5	31.6 // 11.8	9.0 // 34.9	9.0 // 32.6	34.7	30.8
	H-[Ga]- BEA	-7.9	1.9	30.3 // 41.2	27.1 // 13.9	9.1 // 29.3	8.7 // 25.8	32.3	18.2
~	H-[Al]-BEA	-7.7	1.7	30.9 // 39.7	23.4 // 13.7	9.6 // 31.2	10.5 // 25.4	32.6	16.3
	Uncatalyzed		7.2	34.2 // 30.9	60.1 // 59.5	49.4 // 58.1	47.4 // 80.1	41.5	70.7
ryl	H-[B]-BEA	-5.4	2.4	29.3 // 32.5	26.0 // 10.2	14.5 // 35.1	6.8 // 37.9	31.7	29.5
MI Metl	H-[Ga]- BEA	-7.9	0.9	28.1 // 36.8	16.8 // 9.3	11.5 // 28.9	7.1 // 24.9	29.0	11.2
	H-[Al]-BEA	-7.7	-0.9	30.1 // 37.4	15.9 // 11.1	12.8 // 26.4	5.3 // 31.7	29.3	9.5
	Uncatalyzed		7.3	33.6 // 30.2	54.7 // 53.8	46.6 // 54.5	48.5 // 80.1	40.9	65.4
	H-[B]-BEA	-3.9	2.8	32.2 // 36.1	25.7 // 9.5	10.2 // 36.0	10.0 // 31.0	35.0	25.4
DMF	H-[Ga]- BEA	-8.8			18.3 // 10.1	9.3 // 27.3	7.5 // 21.3		9.2
	H-[Fe]-BEA	-7.8	-1.9	32.4 // 40.1	17.3 // 10.2	10.0 // 25.7	5.4 // 21.5	30.5	7.6
	H-[Al]-BEA	-6.1	1.0	31.4 // 38.8	13.0 // 11.9	11.5 // 25.5	6.1 // 20.7	32.4	6.5

		Hydrolysis	- 1 H ₂ O β-C Protonation	Nucleophilic Attack		Hydrolysis	- 2 H ₂ O β-C Protonation	Nucleophilic Attack		
	Catalyst	ΔG_{ads}	$\Delta G^{\ddagger}_{forw} // \Delta G^{\ddagger}_{kcal/mol}$	rev	$\Delta G^{\ddagger}_{app.,Hydr.}$	ΔG_{ads}	$\Delta G^{\ddagger}_{\text{forw}} // \Delta G^{\ddagger}$	rev	$\Delta G^{\ddagger}_{app.,Hydr.}$	
	$H_{-}[R]_{-}RFA$	(Keal/1101)		29.6 // 34.3	64 A	(Real/1101)	25.5 // -0.4		(Real/1101) 43.6*	
ив	H-[Ga]-BEA	4.2	23.2 // 4.8	29.4 // 50.7	52.0	11.8	19.5 // 0.1		31.3 [*]	
Fura	H-[Al]-BEA	4.1	20.8 // 5.0	29.6 // 56.4	49.4	11.6	17.2 // 0.0	0.3 // 25.3	28.8	
	H-[B]-BEA	12.7	22.6 // -0.2	23.9 // 45.2	59.4	14.2	29.2 // 5.7		43.4*	
- hyl	H-[Ga]-BEA	8.5	15.6 // 0.3	21.4 // 39.6	45.1	12.9	13.5 // 4.3		26.5*	
MF Non Met	H-[Al]-BEA	7.7	14.8 // 2.2	23.1 // 39.9	43.4	14.0	17.5 // 9.3		31.4*	
	H-[B]-BEA	12.5	17.2 // 1.8	31.7 // 34.2	59.6	12.0	27.3 // 5.3	7.3 // 12.2	41.3	
hyl	H-[Ga]-BEA	2.5	17.9 // 8.9	34.8 // 34.9	46.3	11.2	11.5 // 8.3	13.2 // 11.8	27.6	
MF Met	H-[Al]-BEA	2.9	15.8 // 9.5	35.2 // 34.7	44.4	15.7	11.6 // 7.0	6.3 // 12.1	27.3	
	H-[B]-BEA	8.8	19.1 // 3.3	27.7 // 36.4	52.4	14.5	23.6 // 11.4	9.7 // 18.7	38.1	
	H-[Ga]-BEA	5.7	9.5 // 4.4	27.8 // 36.5	38.7	15.6	10.8 // 11.7	10.4 // 25.1	26.4	
F	H-[Fe]-BEA	7.7	8.5 // 4.7	28.0 // 36.4	39.4	13.9	11.5 // 11.6	9.0 // 18.6	25.4	
DM	H-[Al]-BEA	7.0	8.0 // 5.4	28.1 // 37.4	37.7	14.2	10.9 // 12.6	9.5 // 19.9	25.1	
* Appare	* Apparent activation energies taken from incomplete profile, using only the barrier for β -C protonation									

Table C.3. Reaction profile energies for the hydrolysis of furan, MF, and DMF on B, Ga, Fe, and Al-substituted BEA zeolites.

(keel/mel)	Fur	an	Fu	ran	DN	ИF	DMF	
(KCal/III0I)	[B]-H	-BEA	[Al]-H	I-BEA	[B]-H	-BEA	[Al]-H	I-BEA
Reaction	$\Delta \mathbf{G}^{\ddagger}_{\mathbf{i}}$	$\Delta \mathbf{G}^{\ddagger}$ -i	$\Delta \mathbf{G}^{\ddagger}_{\mathbf{i}}$	$\Delta G^{\ddagger}-i$	$\Delta \mathbf{G}^{\ddagger}_{\mathbf{i}}$	$\Delta \mathbf{G}^{\ddagger}$ -i	$\Delta \mathbf{G}^{\ddagger}_{\mathbf{i}}$	ΔG^{\ddagger} -i
$F + E \rightarrow CA$	40.7	29.9	40.7	29.9	40.7	29.9	40.7	29.9
*F-E → *CA	29.4	35.0	29.8	41.6	32.2	36.1	31.4	38.8
$CA \rightarrow Dehy$ -Int1	57.7	58.2	57.7	58.2	57.7	58.2	57.7	58.2
$Dehy-Int1 \rightarrow Dehy-Int2$	50.0	59.9	50.0	59.9	50.0	59.9	50.0	59.9
$Dehy-Int2 \rightarrow W + A$	47.3	85.1	47.3	85.1	47.3	85.1	47.3	85.1
*CA \rightarrow *Dehy-Int1	30.2	12.3	24.6	13.1	25.7	9.5	13.0	11.9
*Dehy-Int1 \rightarrow *Dehy-Int2	12.6	68.9	10.7	57.6	10.2	36.0	11.5	25.5
*Dehy-Int2 \rightarrow *W-A	38.7	39.5	34.6	39.1	10.0	31.0	6.1	20.7
$*DMF + W \rightarrow *HYD$	40.4	35.5	28.1	28.8	28.3	30.5	18.4	19.9
Adsorption	ΔG	ads	ΔΟ	ads	ΔΟ	ads	ΔΟ	ads
$F + * \rightarrow *F$	-2	.7	-4	.6	-3.9		-6.1	
$E + * \rightarrow *E$	-3	.8	-5	.1	-3.8		-5.1	
$F + E + * \rightarrow *F-E$	4.	3	1	.2	2.8		1.0	
$CA + * \rightarrow *CA$	-9	.5	-18.3		-1	0.5	-16.3	
$A + * \rightarrow *A$	-4	.6	-6	.3	-5	6.6	-8	.0
$W + * \rightarrow *W$	2.7		-8	.6	2	.7	-8	.6
$W + A + * \rightarrow *W-A$	3.	1	-1	0.6	-2	2.4	13	8.2
$HYD + * \rightarrow *HYD$	-4.0		-11.5		-6.1		-8.5	
$THF + * \rightarrow *THF$	-4	.0	-14	4.7	-4.0		-14	4.7
F = Furan/DMF; E = Ethyle	ne; CA =	Oxanorbo	rnene Cy	cloadduc	t; $A = Ar$	omatic (B	enzene/p	-

Table C.4. Reaction barriers and adsorption strengths of uncatalyzed, H-[B]- and H-[Al]-BEA for furan and DMF, used to parameterize the microkinetic model.

F = Furan/DMF; E = Ethylene; CA = Oxanorbornene Cycloadduct; A = Aromatic (Benzene// Xylene); W = Water; HYD = Hydrolysis Product (Butanedial/Hexanedione); THF = Tetrahydrofuran; * = Catalyst Active Site; *i = Adsorbed

Appendix D

TANDEM DIELS-ALDER OF DIMETHYLFURAN AND ETHYLENE AND DEHYDRATION TO PARA-XYLENE CATALYZED BY ZEOTYPIC LEWIS ACIDS – SUPPORTING INFORMATION



Figure D.1. Full ONIOM model. Ball-and-stick representation of the small layer (17T atoms); tubeframe representation of the intermediate layer (17T atoms), and wireframe representation of the real layer (77T atoms) (H – white; Si – gray; O – red, Sn – purple).



Figure D.2. Free energy profiles for the Diels-Alder aromatization of DMF and ethylene in Sn-BEA. (a) Immobile adsorbates. (b) Mobile adsorbates free to undergo translational motion in one dimension. (c) Mobile adsorbates free to undergo translational motion in two dimensions. The uncatalyzed reaction profiles are at the M06-2X/6-311G(d,p) theory level.



Figure D.3. Free energy profiles for the Diels-Alder aromatization of DMF and ethylene in Ti-BEA. (a) Immobile adsorbates. (b) Mobile adsorbates free to undergo translational motion in one dimension. (c) Mobile adsorbates free to undergo translational motion in two dimensions. The uncatalyzed reaction profiles are at the M06-2X/6-311G(d,p) theory level.



Figure D.4. Free energy profiles for the Diels-Alder aromatization of DMF and ethylene in Zr-BEA. (a) Immobile adsorbates. (b) Mobile adsorbates free to undergo translational motion in one dimension. (c) Mobile adsorbates free to undergo translational motion in two dimensions. The uncatalyzed reaction profiles are at the M06-2X/6-311G(d,p) theory level.



Figure D.5. Microkinetic model predicted rates of p-xylene production as a function of acid site concentration, using the M06-2X/6-311G(2df,p) theory level parameterization for the homogeneous Diels-Alder reaction. a) Immobile adsorbates. b) Mobile adsorbates free to undergo translational motion in one dimension. c) Mobile adsorbates free to undergo translational motion in two dimensions. Simulations run at experimental conditions, 250 °C and 37 atm.



Figure D.6. Sensitivity analysis for the formation of p-xylene from DMF and ethylene in open-Sn-BEA with a) immobile adsorbates, b) adsorbates with 1D translation in the pores, and c) adsorbates with 2D translation in the pores; open-Zr-BEA with d) immobile adsorbates, e) adsorbates with 1D translation in the pores, and f) adsorbates with 2D translation in the pores; and closed-Zr-BEA with g) immobile adsorbates, h) adsorbates with 1D translation in the pores, and i) adsorbates with 2D translation in the pores. For all systems considered, the heterogeneous Diels-Alder NSC was less than 0.01 and thereby has been omitted from the figures for clarity. The M06-2X/6-311G(d,p) theory level parameterization has been used for the kinetics of the homogeneous Diels-Alder reaction.

Table D.1. Adsorption strengths and reaction barriers for two different basis sets in the small layer (high-level theory layer). Single-point energy calculations at the M06-2X/Def2TZVP theory level for the small layer were performed on geometries optimized at the M06-2X/[6-311G(d,p),LANL2DZ(Sn,Zr,Ti)] theory level for the small layer The intermediate and real (low-theory) layers were treated as described in the manuscript. We see that the small-layer basis set has minimal effect on the computed energies.

Small layer theory	M06-2X / 6	-311G(2df,p)	with LANL2D	Z ECP for Sn/	Ti/Zr				
	"Closed"			"Open" Le	ewis		"Open" Si	anol	
E+ZPE (kcal/mol)	Sn-BEA	Ti-BEA	Zr-BEA	Sn-BEA	Ti-BEA	Zr-BEA	Sn-BEA	Ti-BEA	Zr-BEA
Ethylene	-4.9	-3.7	-6.7	-7.2	-6.0	-9.6	-6.9	-6.7	-6.7
DMF	-11.6	-11.3	-12.7	-13.8	-12.9	-16.6	-15.2	-16.3	-15.5
Water	-4.4	-2.4	-9.2	-11.0	-7.5	-13.7	-6.2	-4.9	-4.8
p-Xylene	-14.7	-14.4	-15.2	-14.2	-14.0	-16.6	-20.8	-20.8	-20.8
Oxanorbornene	-13.9	-15.9	-22.6	-23.4	-20.0	-28.0	-26.3	-24.8	-25.4
Hexanedione	-13.9	-12.9	-22.3	-21.4	-17.7	-27.7	-20.0	-19.3	-19.1
Heptane	-16.1	-15.9	-16.5	-17.2	-17.6	-18.8	-15.8	-18.4	-18.1
Diels-Alder Barrier	26.1	25.9	25.3	24.0	24.4	24.3	24.1	24.4	24.3
C-O Cleavage Barrier	28.8	35.6	30.1	30.1	27.2	24.5	28.1	37.8	29.8
Small layer theory	M06-2X / I	Def2TZVP // N	106-2X / 6-311	G(2df,p) with 1	LANL2DZ EC	CP for Sn/Ti/Zr	-	-	_
Ethylene	-5.2	-3.8	-6.5	-8.2	-5.5	-8.9	-7.1	-6.8	-6.8
DMF	-11.5	-11.1	-12.2	-14.1	-12.3	-15.6	-15.6	-16.6	-16.0
Water	-4.4	-1.6	-8.3	-11.3	-6.6	-12.3	-5.8	-3.9	-3.9
p-Xylene	-15.0	-14.4	-15.1	-14.8	-14.3	-15.8	-21.4	-21.4	-21.5
Oxanorbornene	-18.4	-16.6	-22.6	-27.2	-19.8	-27.2	-29.2	-26.1	-26.1
Hexanedione	-14.8	-12.9	-22.8	-23.0	-17.9	-27.5	-20.1	-19.5	-19.5
Heptane	-16.8	-16.4	-17.0	-17.9	-18.3	-19.4	-16.1	-18.9	-18.8
Diels-Alder Barrier	25.7	25.4	25.0	24.0	24.3	24.4	24.6	24.3	24.4
C-O Cleavage Barrier	29.1	34.9	29.3	29.3	26.0	24.0	26.8	37.2	29.7
Average Difference	-0.7	-0.1	-0.1	-1.0	0.0	0.4	-0.5	-0.3	-0.2

	Sn-BEA '	'Closed''	Ti-BE.	A "Closed"	Zr-BEA	"Closed"
Reaction	$\Delta G^{\ddagger}{}_{i}{}^{a}$	$\Delta G^{\ddagger}_{-i}{}^{a}$	$\Delta G^{\ddagger}_{i}{}^{a}$	$\Delta G^{\ddagger}_{-i}{}^{a}$	$\Delta G^{\ddagger}{}_{i}{}^{a}$	$\Delta \mathbf{G}^{\ddagger}_{-\mathbf{i}^{\mathbf{a}}}$
$DMF + E \rightarrow CA$	37.6	30.5	37.6	30.5	37.6	30.5
$*DMF-E \rightarrow *CA$	29.5	26.7°	27.1	26.3°	27.8	30.4°
$CA \rightarrow Dehy$ -Intl	52.7	46.5	52.7	46.5	52.7	46.5
$Dehy$ -Int1 \rightarrow $Dehy$ -Int2	40.2	51.7	40.2	51.7	40.2	51.7
$Dehy$ - $Int2 \rightarrow W + pX$	48.6	90.7	48.6	90.7	48.6	90.7
$*CA \rightarrow *Dehy-Intl$	32.3	36.7	36.0	37.7	28.5	33.1
$Dehy-Int1 \rightarrow Dehy-Int2$	34.6	44.2	37.1	44.0	34.0	39.4
$*Dehy$ -Int2 $\rightarrow *W$ -pX	27.7	50.0 ^c	34.4	62.9 ^c	27.0	56.5°
$*DMF + W \rightarrow *HDI$	50.8	53.1	50.8	53.1	50.8	53.1
Adsorption	$\Delta H_{ads}{}^{a}$	-AS _{ads} (No/1D/2D) ^b	$\Delta H_{ads}{}^{a}$	- $\Delta S_{ads} (No/1D/2D)^b$	$\Delta H_{ads}{}^{a}$	-AS _{ads} (No/1D/2D) ^b
$DMF + * \rightarrow *DMF$	-12.6	40.3 / 28.1 / 17.9	-12.3	39.8 / 27.6 / 17.4	-13.7	39.9 / 27.7 / 17.5
$E + * \rightarrow *E$	-5.2	27.1 / 16.1 / 7.1	-4.0	26.9 / 15.9 / 6.9	-6.8	28.3 / 17.3 / 8.3
$DMF + E + * \rightarrow *DMF - E$	-19.3	69.2 / 56.7 / 46.3	-19.1	73.6 / 61.2 / 50.7	-20.6	70.4 / 58.0 / 47.5
$CA + * \rightarrow *CA$	-27.0	40.9 / 28.5 / 18.0	-25.5	39.9 / 27.4 / 17.0	-34.7	44.8 / 32.4 / 22.0
$pX + * \rightarrow *pX$	-20.9	40.5 / 28.1 / 17.6	-18.7	41.1 / 28.7 / 18.2	-26.2	40.7 / 28.2 / 17.8
$W + * \rightarrow *W$	-27.2	36.1 / 23.6 / 13.2	-23.4	37.9 / 25.5 / 15.0	-30.1	38.4 / 25.9 / 15.5
$W + pX + * \rightarrow *W - pX$	-15.9	42.2 / 30.0 / 19.7	-15.6	41.9 / 29.6 / 19.3	-16.4	43.6 / 31.3 / 21.0
$HDI + * \rightarrow *HDI$	-5.0	26.5 / 16.0 / 7.5	-2.9	25.6 / 15.1 / 6.5	-9.7	27.1 / 16.6 / 8.1
$HEPT + * \rightarrow *HEPT$	-27.8	69.0 / 56.6 / 46.1	-26.9	65.9 / 53.4 / 43.0	-35.3	65.4 / 52.9 / 42.5

Table D.2. Microkinetic model reaction barriers and adsorption strengths in "closed" Sn-, Ti-, and Zr-BEA. at experimental conditions of 250°C and 550 psi. The uncatalyzed, homogeneous Diels-Alder reaction is parameterized at the CBS-QB3 theory level.

^a kcal/mol; ^b cal/mol K, No, 1D, and 2D represent entropy contributions to molecules treated as immobile, or with 1D or 2D translational degrees of freedom within zeolite pores, respectively; ^c Values corrected to equate the free energies of reaction of the homogeneous and heterogeneous systems

	Sn-BEA	``Open'' Silanol	Sn-BEA	• "Open" Lewis	Zr-BEA	``Open'' Silanol	Zr-BEA	"Open" Lewis
Reaction	$\Delta G^{\ddagger_i^a}$	ΔG^{\ddagger}_{-i}	$\Delta G^{\ddagger_i^a}$	$\Delta G^{\ddagger} \cdot i^{a}$	$\Delta G^{\ddagger_i^a}$	ΔG^{\ddagger}_{-i}	$\Delta G^{\ddagger_i^a}$	$\Delta G^{\ddagger}-i^{a}$
$*DMF-E \rightarrow *CA$	29.6	38.2c	27.6	29.7c	29.1	37.2c	28.4	31.9c
$*CA \rightarrow *Dehy-Intl$	28.7	5.7	22.7	26.6	30.3	5.2	24.4	28.7
$*Dehy$ -Int $l \rightarrow *Dehy$ -Int 2	9.2	36.3	28.9	36.0	8.4	38.1	30.2	36.9
$*Dehy$ -Int2 $\rightarrow *W$ -pX	16.0	38.7c	20.8	46.1c	19.9	43.1c	24.4	51.7c
$*DMF + W \rightarrow *HDI$	28.4	30.7			32.9	33.5		
Adsorption	$\Delta H_{ads}{}^{a}$	-ASads (No/1D/2D) ^b	$\Delta H_{ads}{}^{a}$	-ASads (No/1D/2D) ^b	$\Delta H_{ads}{}^{a}$	-ASads (No/1D/2D) ^b	$\Delta H_{ads}{}^{a}$	-ASads (No/1D/2D) ^b
$DMF + * \rightarrow *DMF$	-16.5	38.8 / 26.6 / 16.4	-14.6	41.4 / 29.2 / 19.0	-16.9	39.1 / 26.9 / 16.7	-17.1	42.0 / 29.9 / 19.7
$E + * \rightarrow *E$	-7.4	27.3 / 16.3 / 7.4	-7.4	28.1 / 17.1 / 8.1	-7.2	27.3 / 16.3 / 7.3	-9.7	30.0 / 19.0 / 10.0
$DMF + E + * \rightarrow *DMF - E$	-22.6	67.0 / 54.6 / 44.1	-21.4	70.9 / 58.4 / 48.0	-22.2	66.9 / 54.4 / 44.0	-24.4	71.1 / 58.7 / 48.2
$CA + * \rightarrow *CA$	-38.4	40.9 / 28.5 / 18.0	-36.5	45.3 / 32.9 / 22.4	-37.6	40.9 / 28.5 / 18.0	-39.6	44.6 / 32.2 / 21.8
$pX + * \rightarrow *pX$	-2.8	36.2 / 23.8 / 13.3	-26.1	41.5 / 29.0 / 18.6	-0.3	40.9 / 28.5 / 18.0	-31.0	41.0 / 28.6 / 18.1
$W + * \rightarrow *W$	-28.0	36.3 / 23.9 / 13.4	-31.2	39.4 / 27.0 / 16.5	-27.9	36.8 / 24.3 / 13.9	-34.7	37.8 / 25.3 / 14.9
$W + pX + * \rightarrow *W - pX$	-22.1	41.5 / 29.2 / 18.9	-15.7	40.1 / 27.9 / 17.6	-22.1	42.3 / 30.0 / 19.7	-17.6	42.8 / 30.5 / 20.2
$HDI + * \rightarrow *HDI$	-7.0	25.5 / 15.0 / 6.5	-11.5	27.3 / 16.8 / 8.2	-5.3	23.1 / 12.5 / 4.0	-14.0	26.7 / 16.2 / 7.6
$HEPT + * \rightarrow *HEPT$	-28.4	66.3 / 53.9 / 43.4	-35.2	70.5 / 58.1 / 47.7	-27.8	66.7 / 54.2 / 43.8	-40.3	69.7 / 57.3 / 46.8

Table D.3. Microkinetic model reaction barriers and adsorption strengths in "open" Sn-, Ti-, and Zr-BEA at experimental conditions of 250°C and 550 psi. The uncatalyzed, homogeneous Diels-Alder reaction is parameterized at the CBS-QB3 theory level.

^a kcal/mol; ^b cal/mol K, No, 1D, and 2D represent entropy contributions to molecules treated as immobile, or with 1D or 2D translational degrees of freedom within zeolite pores, respectively; ^c Values corrected to equate the free energies of reaction of the homogeneous and heterogeneous systems

Table D.4. Microkinetic model reaction barriers in "closed" Sn-, Ti-, and Zr-BEA, at experimental conditions of 250°C and 550 psi. The uncatalyzed, homogeneous Diels-Alder reaction is parameterized at the M06-2X/6-311G(2df,p) theory level.

(kcal/mol)	Sn-BEA	"Closed"	Ti-BEA	"Closed"	Zr-BEA	"Closed"
Reaction	$\Delta G^{\ddagger}_{i}{}^{a}$	$\Delta G^{\ddagger}-i^{a}$	$\Delta G^{\ddagger}_{i}{}^{a}$	$\Delta G^{\ddagger}-i^{a}$	$\Delta G^{\ddagger}_{i}{}^{a}$	ΔG^{\ddagger} -i ^a
$DMF + E \rightarrow CA$	40.6	29.6	40.6	29.6	40.6	29.6
$*DMF-E \rightarrow *CA$	29.5	30.7	27.1	30.4	27.8	33.6
$CA \rightarrow Dehy$ -Intl	58.1	57.1	58.1	57.1	58.1	57.1
$Dehy$ -Int1 \rightarrow $Dehy$ -Int2	48.2	56.0	48.2	56.0	48.2	56.0
$Dehy$ - $Int2 \rightarrow W + pX$	49.2	85.3	49.2	85.3	49.2	85.3
$*CA \rightarrow *Dehy-Intl$	32.3	36.7	36.0	37.7	28.5	33.1
$*Dehy$ -Int1 \rightarrow $*Dehy$ -Int2	34.6	44.2	37.1	44.0	34.0	39.4
$*Dehy-Int2 \rightarrow *W-pX$	27.7	55.7	34.4	68.5	27.0	60.6
$*DMF + W \rightarrow *HDI$	50.8	51.6	50.8	51.6	50.8	51.6

Table D.5. Microkinetic model reaction barriers in "open" Sn-, Ti-, and Zr-BEA, at experimental conditions of 250°C and 550 psi. The uncatalyzed, homogeneous Diels-Alder reaction is parameterized at the M06-2X/6-311G(2df,p) theory level.

(kcal/mol)	Sn-BEA "Open"	Silanol	Sn-BEA "Open"	Lewis	Zr-BEA "Open"	Silanol	Zr-BEA "Open" Lewis	
Reaction	$\Delta G^{\ddagger}_{i}{}^{a}$	$\Delta G^{\ddagger} \cdot i^a$	$\Delta G^{\ddagger_i a}$	$\Delta G^{\ddagger}_{-i}{}^{a}$	$\Delta G^{\ddagger_i a}$	$\Delta G^{\ddagger}-i^{a}$		
$*DMF-E \rightarrow *CA$	29.6	38.2	27.6	30.8	29.1	37.2	28.4	35.8
$*CA \rightarrow *Dehy-Intl$	28.7	5.7	22.7	26.6	30.3	5.2	24.4	28.7
$*Dehy-Int1 \rightarrow *Dehy-Int2$	9.2	36.3	28.9	36.0	8.4	38.1	30.2	36.9
$*Dehy-Int2 \rightarrow *W-pX$	16.0	43.6	20.8	50.3	19.9	49.0	24.4	57.0
$*DMF + W \rightarrow *HDI$	28.2	30.7			32.7	33.5		

		[DMF]	a,2			[DMF *] ^{a,2}	2	rDA,Homo.3		rDA,Hetero.3	
	k _{DA,Homo} . ¹	1 mM	12 mM	[E] ^{a,2}	k _{DA,Hetero} . ¹	1 mM	12 mM	1 mM	12 mM	1 mM	12 mM
Sn-BEA "Closed" 0D			1.4		1.6x10 ⁻³	3.9x10 ⁻⁷	4.7x10 ⁻⁶	1.92	x10 ⁻⁴	4.0 x 10 ⁻¹¹	4.8 x 10 ⁻¹⁰
Sn-BEA "Closed" 1D	2.1x10 ⁻³		1.4	0.064	1.8x10 ⁻³	2.3x10 ⁻⁵	2.8x10 ⁻⁴	1.92	x10 ⁻⁴	2.7 x 10 ⁻⁹	3.3 x 10 ⁻⁸
Sn-BEA "Closed" 2D			1.4		9.3x10 ⁻⁵	2.6x10 ⁻⁵	3.2x10 ⁻⁴	1.92	x10 ⁻⁴	1.6 x 10 ⁻¹⁰	1.9 x 10 ⁻⁹
Ti-BEA "Closed" 0D			1.4		1.4x10 ⁻³	4.0x10 ⁻⁷	4.8x10 ⁻⁶	1.92	x10 ⁻⁴	3.6 x 10 ⁻¹¹	4.3 x 10 ⁻¹⁰
Ti-BEA "Closed" 1D	2.1x10 ⁻³		1.4	0.064	1.6x10 ⁻³	3.0x10 ⁻⁵	3.6x10 ⁻⁴	1.92	x10 ⁻⁴	3.1 x 10 ⁻⁹	3.7 x 10 ⁻⁸
Ti-BEA "Closed" 2D			1.4		8.0x10 ⁻⁵	3.5x10 ⁻⁵	4.2x10 ⁻⁴	1.92	x10 ⁻⁴	1.8 x 10 ⁻¹⁰	2.1 x 10 ⁻⁹
Zr-BEA "Closed" 0D		1.4	1.3		4.3x10 ⁻³	1.4x10 ⁻⁶	1.6x10 ⁻⁵	3.7 x 10 ⁻¹⁰	4.1x10 ⁻⁹	3.7 x 10 ⁻¹⁰	4.1 x 10 ⁻⁹
Zr-BEA "Closed" 1D	2.1x10 ⁻³	1.2	1.0	0.064	4.9x10 ⁻³	1.7x10 ⁻⁵	4.6x10 ⁻⁴	5.2 x 10 ⁻⁹	1.4x10 ⁻⁸	5.2 x 10 ⁻⁹	1.4 x 10 ⁻⁸
Zr-BEA "Closed" 2D		1.2	1.0		7.0x10 ⁻⁵	1.5x10 ⁻⁵	4.4x10 ⁻⁴	6.7 x 10 ⁻¹¹	1.8x10 ⁻¹⁰	6.7 x 10 ⁻¹¹	1.8 x 10 ⁻¹⁰
Sn-BEA "Open" 0D		0.61	0.19		7.2x10 ⁻³	1.4x10 ⁻⁶	2.5x10 ⁻⁴	3.8 x 10 ⁻⁹	1.2x10 ⁻⁸	3.8 x 10 ⁻⁹	1.2 x 10 ⁻⁸
Sn-BEA "Open" 1D	2.1x10 ⁻³	0.26	0.14	0.064	8.2x10 ⁻³	1.4x10 ⁻⁵	6.2x10 ⁻⁴	3.1 x 10 ⁻⁹	2.0x10 ⁻⁸	3.1 x 10 ⁻⁹	2.0 x 10 ⁻⁸
Sn-BEA "Open" 2D		0.25	0.14		1.0x10 ⁻⁴	1.4x10 ⁻⁵	6.0x10 ⁻⁴	3.6 x 10 ⁻¹¹	2.4x10 ⁻¹⁰	3.6 x 10 ⁻¹¹	2.4 x 10 ⁻¹⁰
Zr-BEA "Open" 0D		0.45	0.17		6.8x10 ⁻³	4.6x10 ⁻⁶	2.6x10 ⁻⁴	3.2 x 10 ⁻⁹	1.4x10 ⁻⁸	3.2 x 10 ⁻⁹	1.4 x 10 ⁻⁸
Zr-BEA "Open" 1D	2.1x10 ⁻³	0.40	0.16	0.064	7.8x10 ⁻³	9.8x10 ⁻⁶	9.8x10 ⁻⁴	7.2 x 10 ⁻⁹	3.7x10 ⁻⁸	7.2 x 10 ⁻⁹	3.7 x 10 ⁻⁸
Zr-BEA "Open" 2D		0.40	0.16		1.2x10 ⁻⁵	9.4x10 ⁻⁶	9.5x10 ⁻⁴	1.1 x 10 ⁻¹¹	5.6x10 ⁻¹¹	1.1 x 10 ⁻¹¹	5.6 x 10 ⁻¹¹

Table D.6. Kinetic analysis of the homogeneous run at a CBS-QB3 (r_{DA,Homo}) and heterogeneous Diels-Alder reaction (r_{DA,Hetero}) in the different catalytic systems.

^a Species concentrations taken as the average value from the MKM run over 24 hours with 1 and 12 mM catalyst loadings, as indicated; where only one value is shown, no difference was seen between the average values of the two catalyst loading cases ${}^{1} M^{-1} s^{-1}; {}^{2} M; {}^{3} M s^{-1}$

		[DMF]	a,2			[DMF*] ^{a,2}		rDA,Homo.3		rDA,Hetero. ³	
	k _{DA,Homo} . ¹	1 mM	12 mM	[E] ^{a,2}	k _{DA,Hetero} . ¹	1 mM	12 mM	1 mM	12 mM	1 mM	12 mM
Sn-BEA "Closed" 0D			1.4		1.6x10 ⁻³	3.9x10 ⁻⁷	4.7x10 ⁻⁶	1.0	x10 ⁻⁵	4.0x10 ⁻¹¹	4.8x10 ⁻¹⁰
Sn-BEA "Closed" 1D	1.1x10 ⁻⁴		1.4	0.064	1.8x10 ⁻³	2.3x10 ⁻⁵	2.8x10 ⁻⁴	1.0	x10 ⁻⁵	2.7x10 ⁻⁹	3.3x10 ⁻⁸
Sn-BEA "Closed" 2D			1.4		9.3x10 ⁻⁵	2.6x10 ⁻⁵	3.1x10 ⁻⁴	1.0	x10 ⁻⁵	1.6x10 ⁻¹⁰	1.9x10 ⁻⁹
Ti-BEA "Closed" 0D			1.4		1.4x10 ⁻³	4.0x10 ⁻⁷	4.8x10 ⁻⁶	1.0	x10 ⁻⁵	3.6x10 ⁻¹¹	4.3x10 ⁻¹⁰
Ti-BEA "Closed" 1D	1.1x10 ⁻⁴		1.4	0.064	1.6x10 ⁻³	3.0x10 ⁻⁵	3.6x10 ⁻⁴	1.0	x10 ⁻⁵	3.1x10 ⁻⁹	3.7x10 ⁻⁸
Ti-BEA "Closed" 2D			1.4		8.0x10 ⁻⁵	3.5x10 ⁻⁵	4.2x10 ⁻⁴	1.0	x10 ⁻⁵	1.8x10 ⁻¹⁰	2.1x10 ⁻⁹
Zr-BEA "Closed" 0D			1.4		4.3x10 ⁻³	1.4x10 ⁻⁶	1.6x10 ⁻⁵	1.0	x10 ⁻⁵	3.7x10 ⁻¹⁰	4.5x10 ⁻⁹
Zr-BEA "Closed" 1D	1.1x10 ⁻⁴	1.4	1.3	0.064	4.9x10 ⁻³	4.5x10 ⁻⁴	4.5x10 ⁻⁴	2.0x10 ⁻⁸	9.6x10 ⁻⁶	2.0x10 ⁻⁸	1.4x10 ⁻⁷
Zr-BEA "Closed" 2D		1.4	1.3		7.0x10 ⁻⁵	4.3x10 ⁻⁴	4.3x10 ⁻⁴	3.1x10 ⁻¹⁰	9.5x10 ⁻⁶	3.1x10 ⁻¹⁰	1.9x10 ⁻⁹
Sn-BEA "Open" 0D		1.3	1.1		7.2x10 ⁻³	2.4x10 ⁻⁴	2.4x10 ⁻⁴	1.3x10 ⁻⁸	8.2x10 ⁻⁶	1.3x10 ⁻⁸	1.1x10 ⁻⁷
Sn-BEA "Open" 1D	1.1x10 ⁻⁴	1.1	0.96	0.064	8.2x10 ⁻³	6.0x10 ⁻⁴	6.0x10 ⁻⁴	4.1x10 ⁻⁸	7.0x10 ⁻⁶	4.1x10 ⁻⁸	3.2x10 ⁻⁷
Sn-BEA "Open" 2D		1.1	0.96		1.0x10 ⁻⁴	5.8x10 ⁻⁴	5.8x10 ⁻⁴	4.8x10 ⁻¹⁰	7.0x10 ⁻⁶	4.8x10 ⁻¹⁰	3.9x10 ⁻⁹
Zr-BEA "Open" 0D		1.2	0.98		6.8x10 ⁻³	2.6x10 ⁻⁴	2.6x10 ⁻⁴	1.2x10 ⁻⁸	7.2x10 ⁻⁶	1.2x10 ⁻⁸	1.1x10 ⁻⁷
Zr-BEA "Open" 1D	1.1x10 ⁻⁴	1.1	0.96	0.064	7.8x10 ⁻³	9.6x10 ⁻⁴	9.6x10 ⁻⁴	5.0x10 ⁻⁸	7.0x10 ⁻⁶	5.0x10 ⁻⁸	4.8x10 ⁻⁷
Zr-BEA "Open" 2D		1.1	0.96		1.2x10 ⁻⁵	9.3x10 ⁻⁴	9.3x10 ⁻⁴	7.6x10 ⁻¹¹	7.0x10 ⁻⁶	7.6x10 ⁻¹¹	7.3x10 ⁻¹⁰

Table D.7. Kinetic analysis of the homogeneous run at an M06-2X/6-311G(2df,p) theory level (r_{DA,Homo}) and heterogeneousDiels-Alder reaction (r_{DA,Hetero}) in the different catalytic systems.

^a Species concentrations taken as the average value from the MKM run over 24 hours with 1 and 12 mM catalyst loadings, as indicated; where only one value is shown, no difference was seen between the average values of the two catalyst loading cases ${}^{1}M^{-1}s^{-1}$; ${}^{2}M$; ${}^{3}M s^{-1}$

Appendix E

CHARACTERIZATION OF THE AROMATIZATION OF OXYGENATED FURANS BY FRAMEWORK ZINC IN ZEOLITES USING FIRST PRINCIPLES CALCULATIONS – SUPPORTING INFORMATION

Table E.1.	Zn-substitution	energies**	into	the	different	T-sites	of	BEA	zeolites
	(kcal/mol).								

Active Site			Z0					Z2		
Sphere Size	4 Å	5 Å	6 Å	7 Å	8 Å	4 Å	5 Å	6 Å	7 Å	8 Å
<i>T1</i>	38.7	16.2	19.3	11.6	15.4	38.7	16.2	19.3	11.6	15.4
T2	39.0	15.5	18.9	13.6	17.6	39.0	15.5	18.9	13.6	17.6
<i>T3</i>	42.8	23.4	29.8	17.1	15.7	42.8	23.4	29.8	17.1	15.7
T4	42.2	23.0	30.0	15.9	15.0	42.2	23.0	30.0	15.9	15.0
<i>T5</i>	36.5	9.1	11.0	15.4	6.1	36.5	9.1	11.0	15.4	6.1
<i>T6</i>	40.2	9.9	12.7	11.3	3.0	40.2	9.9	12.7	11.3	3.0
<i>T</i> 7	46.5	20.6	25.5	18.0	10.5	46.5	20.6	25.5	18.0	10.5
<i>T</i> 8	46.8	23.4	25.6	12.6	13.2	46.8	23.4	25.6	12.6	13.2
T9	47.0	21.2	24.7	18.2	16.5	47.0	21.2	24.7	18.2	16.5
* Refers to the distance from the substituted Zn atom for included in the given model										
** Substitution energies calculated as $E_{Sub} = [E_{Zn-BEA,Z0/Z2} + E_{Si}] - [E_{Si-BEA} + E_{Zn} + 2E_{H/Li}]$										

		ZO			Z2	
ρ (a.u.)	S1 *	S2**	S3***	S1 *	S2**	S3***
Zn-O4	0.11	0.12	0.11	0.09	0.09	0.09
Zn-O5	0.06	0.05	0.05	0.06	0.06	0.06
Zn-06	0.07	0.07	0.07	0.09	0.09	0.09
Zn-07	0.11	0.11	0.11	0.10	0.11	0.11
O5-H2/Li2	0.34	0.34	0.35	0.03	0.03	0.03
06-H3/Li3	0.35	0.35	0.36	0.05	0.05	0.04
$-\frac{1}{4}\nabla^2(\rho)$						
(a.u.)						
Zn-O4	-0.14	-0.19	-0.18	-0.14	-0.14	-0.11
Zn-O5	-0.07	-0.06	-0.07	-0.07	-0.07	-0.07
Zn-06	-0.08	-0.09	-0.09	-0.13	-0.13	-0.10
Zn-07	-0.13	-0.17	-0.16	-0.16	-0.17	-0.13
O5-H2/Li2	0.51	0.61	0.71	-0.06	-0.06	-0.06
06-H3/Li3	0.51	0.61	0.71	-0.01	-0.06	-0.09
* All stoms use 6.21 $G(d n)$ basis set						

Table E.2. Bader analysis of bond critical points of the local active site. Atom numbering scheme corresponds to that found in Figure 6.4.

* All atoms use 6-31G(d,p) basis set

** Atoms shown in Figure 3 use 6-311G(2df,p) basis set and all remaining atoms use 6-31G(d,p) basis set

*** Atoms shown in Figure 3 use 6-311++G(3df,3pd) basis set and all remaining atoms use 6-31G(d,p) basis set

Appendix F

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